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GAS CHROMATOGRAPHY-MASS SPECTROMETRY FACILITY: RECENT IMPROVEME--ETC(U)  
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Marine organic and organic geochemical studies require the best available performance in trace analysis of organic compounds in environmental samples. This report briefly outlines some of the recent improvements in the experimental capabilities of the Chemistry Department Gas Chromatography/Mass Spectrometry Facility (GC/MS Facility) from a user-oriented and non-technical viewpoint. These improvements include principally the interfacing of high performance glass capillary columns with Finnigan 1015 and 3200 quadrupole		

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by

Nelson M. Frew  
and  
Richard M. Sawdo

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TECHNICAL REPORT

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GAS CHROMATOGRAPHY-MASS SPECTROMETRY FACILITY:

RECENT IMPROVEMENTS AND APPLICATIONS

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## ABSTRACT

Marine organic and organic geochemical studies require the best available performance in trace analysis of organic compounds in environmental samples. This report briefly outlines some of the recent improvements in the experimental capabilities of the Chemistry Department Gas Chromatography/Mass Spectrometry Facility (GC/MS Facility) from a user-oriented and non-technical viewpoint. These improvements include principally the interfacing of high performance glass capillary columns with Finnigan 1015 and 3200 quadrupole mass spectrometers, and the adaptation of the latter for use with selective chemical ionization (CI) techniques. Some of the new capabilities available using combined glass capillary GC/EI-MS and CI-MS are illustrated with examples from research in several areas of marine organic chemistry. These include studies of volatile organics in seawater, the distributions of various lipid class compounds in marine phytoplankton, sediments and particulate matter, and the behavior of anthropogenic pollutants in natural and artificial marine ecosystems.

## INTRODUCTION

The samples encountered in marine organic chemistry and geochemistry are among the most complex and difficult mixtures to analyze. Consequently, advances in the field are frequently tied to advances in organic analytical capabilities. Over the last few years, very rapid development in the capability of dealing with many components in these mixtures has occurred, principally due to three technical advances:

- (1) The availability of high resolution glass capillary columns and chromatographic equipment suitable for their routine use.
- (2) The availability of sensitive quadrupole mass spectrometers with associated computer controlled data acquisition and data manipulation capability.
- (3) The availability of new selective ionization techniques such as chemical ionization (CI).

These three developments, while individually significant, are particularly effective when combined into systems that permit the high resolution separation of a complex sample, its analysis by mass spectrometry with electron impact (EI) or chemical ionization (CI), and the subsequent manipulation and display of the structural information via a data system.

Since 1975, considerable effort has been invested in upgrading our Finnigan quadrupole mass spectrometers to a state-of-the-art level with respect to combined high resolution gas chromatography-mass spectrometry operations. Previous analytical work with these instruments had been limited to low resolution (packed column) GC/MS analyses (see, for example, GAGOSIAN, 1975; FARRINGTON and TRIPP, 1977; FARRINGTON et al., 1977a,b), or to low voltage EI probe distillation analyses, such as determinations of homolog distributions for aromatic hydrocarbons (BLUMER, 1975a,b; BLUMER and YOUNGBLOOD, 1975; SAWDO and BLUMER, 1976;

BLUMER and DORSEY, 1977). The analyses of various types of complex samples derived from the marine environment, however, required the development of a chromatographic capability with the highest possible resolution and sensitivity. In addition, the full utilization of ionization techniques such as chemical ionization required a high degree of compatibility between chromatographic and CI operating conditions. In this report, we describe the instrumental modifications and improvements designed to meet these requirements, along with examples of applications to marine organic chemistry studies.

#### Glass Capillary Chromatography

Despite the introduction of open tubular columns two decades ago (GOLAY, 1958), the adoption of capillary gas chromatography in marine organic chemistry as well as other fields has been slow due to a lack of optimal instrumentation and reproducible methods for making capillary columns of high quality (KAISER, 1974, 1975; GROB, 1975, 1979). Particularly for marine chemistry studies, where frequently only trace quantities of material are available for analysis, capillary columns must meet stringent requirements in addition to that of high resolution. These include:

- (1) High liquid film stability and, therefore, low bleeding at elevated temperatures.
- (2) A lack of active sites for irreversible adsorption or catalytic decomposition of materials analyzed even at the low nanogram or picogram level.
- (3) High durability, as evidenced by lack of sensitivity to solvent or component overloading, moisture, and other factors.
- (4) High reproducibility of performance characteristics from column to column.

Numerous procedures for fabrication of capillary columns have been reported in the literature (BADINGS et al., 1975; GORETTI et al., 1975; ROERADE, 1975;



SCHOMBURG and HUSMANN, 1975; FRANKEN et al., 1976; SCHULTE, 1976). Many of these techniques fail to meet one or more of the above mentioned criteria and thus, have found only limited application. In our experience, however, the glass capillary coating techniques developed within the last few years by Grob (GROB and GROB, 1976; GROB et al., 1977, 1978, 1979) do satisfy these requirements to a high degree and we have adopted them for a wide variety of applications.

Two principal methods, developed and refined by Grob, are employed for treating the glass surface prior to coating with the stationary phase. The first method involves the leaching of either soft or borosilicate glass with hydrochloric acid at elevated temperature, followed by precoating the glass surface with a thin layer of barium carbonate crystals bonded directly to the glass (GROB and GROB, 1976). Undesirable properties of the glass are thereby masked, and the effects of variations in glass composition are minimized. Further, the degree of surface roughness required for strong liquid phase adhesion can be varied according to the liquid phase polarity by controlling the barium carbonate deposition rate and, hence, crystal size.

The second method involves a more vigorous acid leaching of the glass followed by dehydration, and an extended vapor phase silanization of the resultant silica surface (WELSCH et al., 1977; GROB et al., 1979b). This technique produces an extremely inert surface on which apolar coatings remain stable at very high temperatures ( $\leq 350^{\circ}\text{C}$ ). These "high temperature" apolar columns extend the boiling point range of compounds which can be successfully chromatographed to compounds containing 50-60 carbons, when used with on-column injection (GROB and GROB, 1979).

The adoption of these capillary coating techniques represents a major advance in the analytical capabilities of the GC/MS Facility. Our experience

in the routine preparation of high quality, durable capillary columns now extends over a four year period. A laboratory has been equipped for in-house production of both types of columns. These columns typically exhibit low bleed and adsorptive properties and high efficiency. Figure 1, for example, is a glass capillary chromatogram of Aroclor 1254, a complex mixture of polychlorinated biphenyls. This excellent separation was performed on a 25 meter SE-52 column prepared by the high temperature silanization technique. The column exhibited no discernible bleed at the final analysis temperature (270°C).

Barium carbonate precoated columns have proven to be extremely durable, providing sustained performance with daily use for periods of a year or more. As an example, the original test chromatogram for a barium carbonate type SE-52 column is shown in Figure 2. For comparison, a test chromatogram (Figure 3) was made after twelve months of frequent use employing a more comprehensive test (GROB, JR. et al., 1978). As shown by that test, the column continued to provide excellent resolution and showed little increase in adsorption of representative polar compounds such as 1-octanol despite continuous heavy use. The durability of the high temperature silanized columns over a long period has not yet been fully evaluated in our laboratory since the technique is very recent.

The gas chromatographs for both the Finnigan 1015 and 3200 GC/MS systems at the facility have been modified to accommodate glass capillary columns and to use the splitless injection technique of Grob (GROB and GROB, 1969; GROB and GROB, JR., 1978). The splitless technique improves the resolution of low boiling components adjacent to the solvent peak due to the solvent effect (GROB and GROB, JR., 1974) and allows large injection volumes (1-3 microliters). The latter feature is a significant advantage in the analysis of dilute samples since the sample can be more fully utilized. Splitless injection has been used exclusively for both GC/EI-MS and GC/CI-MS.

FIGURE 1. Glass capillary chromatogram of polychlorinated biphenyls in Aroclor 1254 (Monsanto Corp., St. Louis, Missouri). Column: SE-52 (high temperature), 25 meters x 0.32 mm. Gas chromatographic conditions: Carlo Erba Model 4160; on-column injector, 25°C; flame ionization detector, 300°C; H<sub>2</sub> carrier, 0.3 kg/cm<sup>2</sup>; temperature program, 155-270°C at 2°C/min. Sample courtesy of A. C. Davis, Woods Hole Oceanographic Institution.

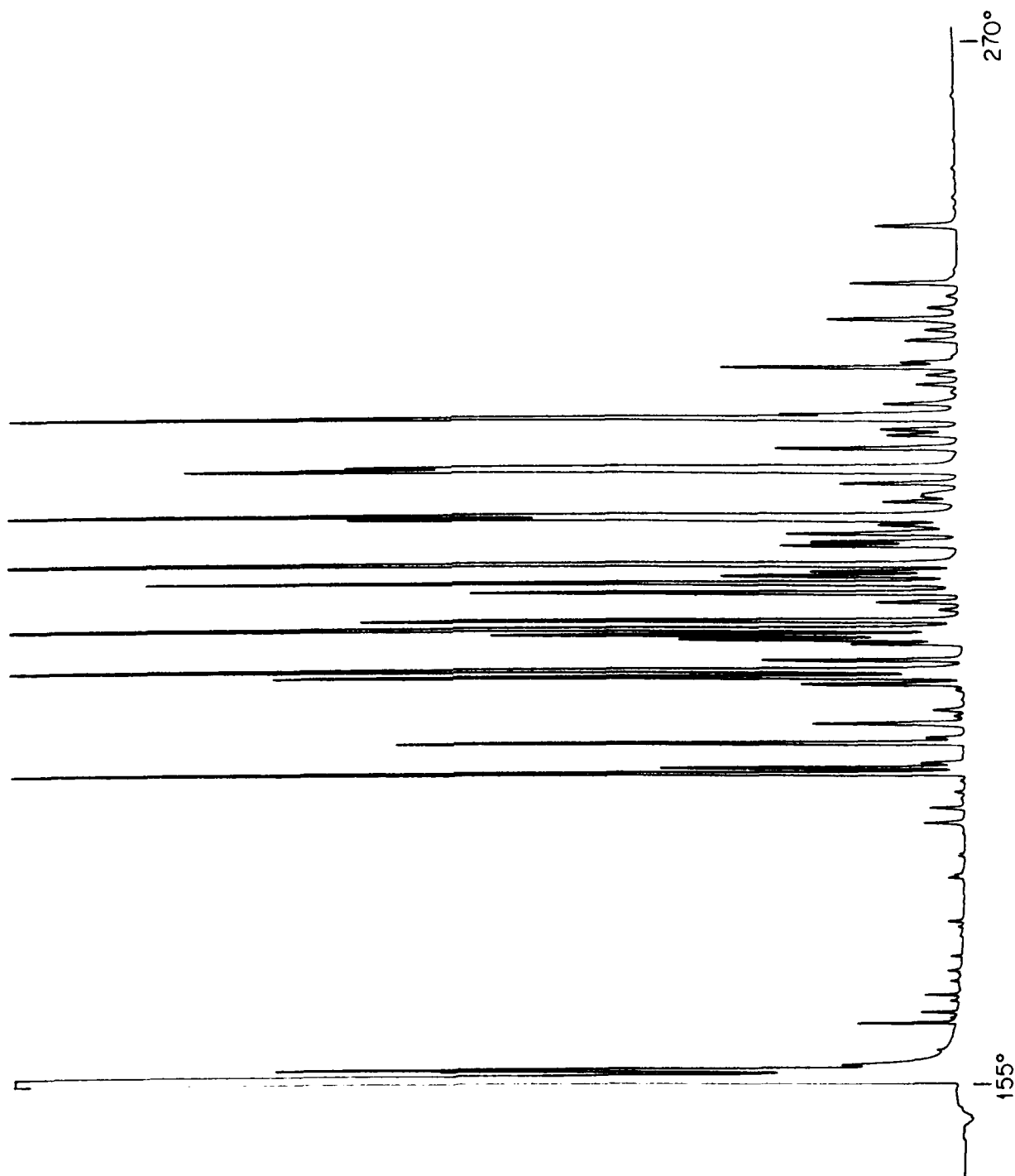


FIGURE 2. Test chromatogram for an apolar capillary column (SE-52) pretreated with barium carbonate. Column dimensions: 27 meters x 0.31 mm. Carrier gas: He at 0.6 atmosphere. Polarity test mixture (GROB, 1971) at 70°C. Trennzahl (TZ) for undecane/dodecane pair is approximately 43.

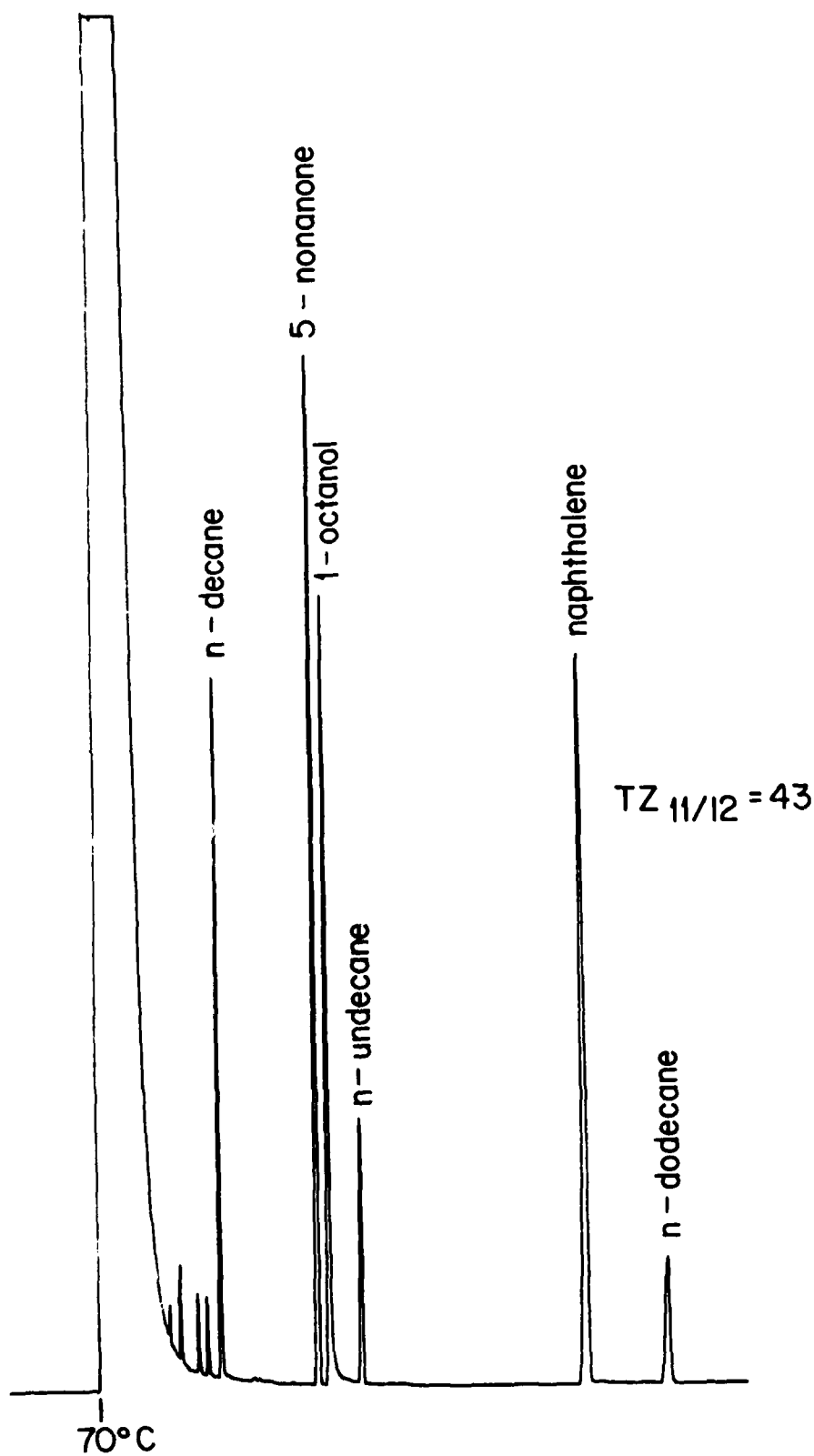
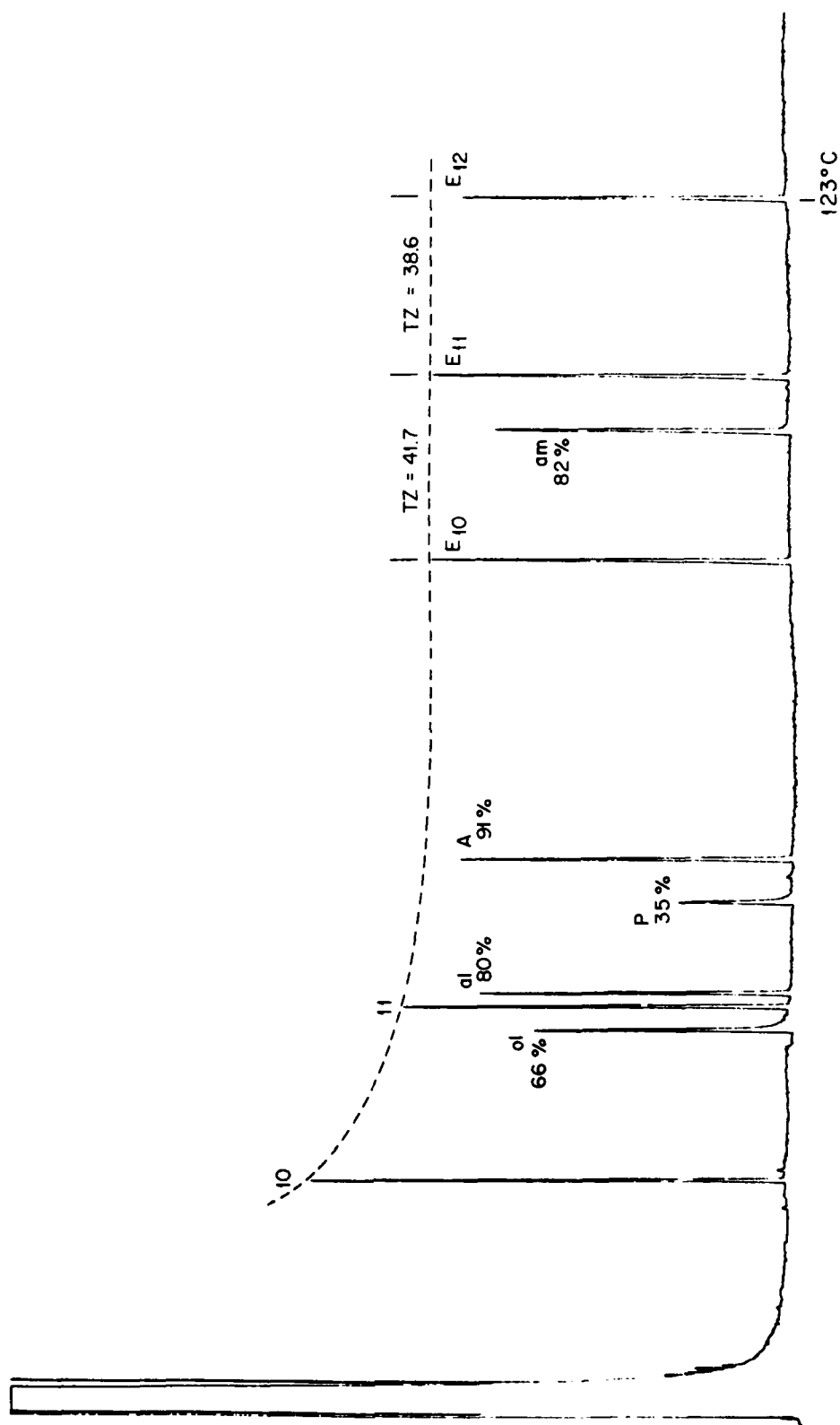


FIGURE 3. Test chromatogram for the same SE-52 column indicated in Figure 2 after twelve months of continuous use. Comprehensive test according to Grob, Jr. et al (1978). Gas chromatographic conditions: Carlo Erba Model 2150; helium carrier, 0.5 atmosphere;  $\text{CH}_4$  retention time, 95 sec.; temperature program, 40-150°C at 1°C/min. Film thickness: 0.16  $\mu\text{m}$ .





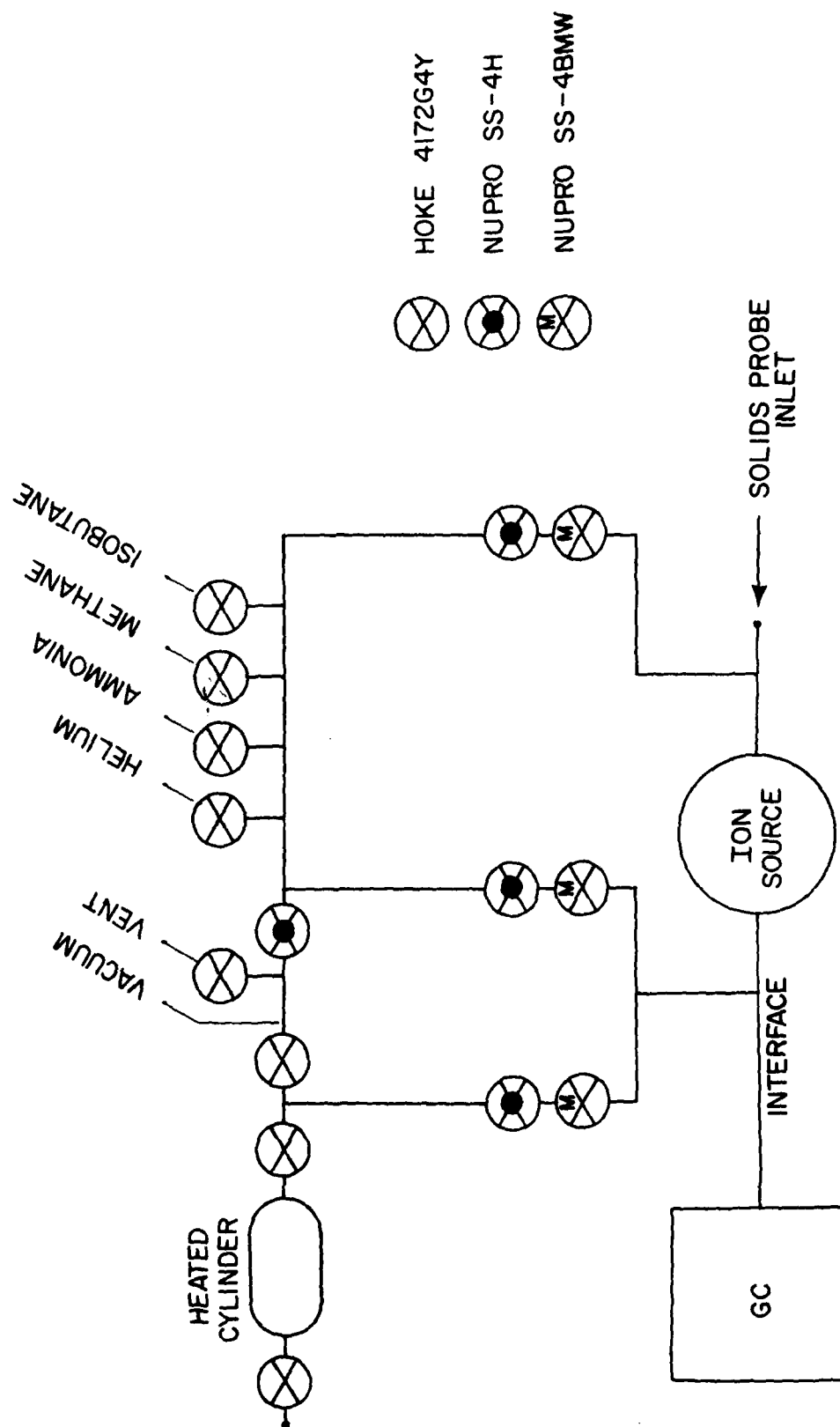
### Chemical Ionization

Chemical ionization, introduced by Munson and Field in 1966 (MUNSON and FIELD, 1966; FIELD, 1968), is a low energy or "soft" ionization process in which sample ions are produced by chemical reactions with an ionized reagent gas.

The Finnigan 3200 mass spectrometer at the facility has been modified to take advantage of the wide range of reagent gases available for chemical ionization. A gas manifold (Figure 4) has been designed which allows separate selection of up to five reactants including corrosive gases such as ammonia and nitric oxide, and using a heated reservoir, liquid reactants such as water and methanol. The use of mixed reagent gases (HUNT and RYAN, 1972; HUNT and HARVEY, 1975; HUNT, 1976; JELUS and MUNSON, 1974) such as argon-water, nitrogen-isobutane, and nitric oxide-nitrogen is thereby facilitated. Reactant gas pressure in the ion source can be precisely controlled using stainless steel bellows fine metering valves. Two separate reactant gas entry ports for capillary and probe analyses ensure optimum sensitivity by minimizing back-effusion of sample components away from the source. A list of reagent gases available at the facility and an indication of their potential applications is given in Table 1.

The combination of chemical ionization techniques with glass capillary gas chromatography offers two major advantages in the analysis of the complex mixtures typically encountered in marine geochemistry. First, sensitivity is enhanced due not only to sharpened chromatographic peak shape, but also to a distribution of the total ion signal among fewer fragment ions. A comparison of electron impact and chemical ionization modes for an n-alkane (Figure 5) illustrates the degree to which fragmentation can be reduced by proper selection of the reactant gas, resulting in simplified spectra and improved ability to detect molecular ions in complex mixtures.

FIGURE 4. Schematic diagram of manifold arrangement for selection of various chemical ionization reagent gases.

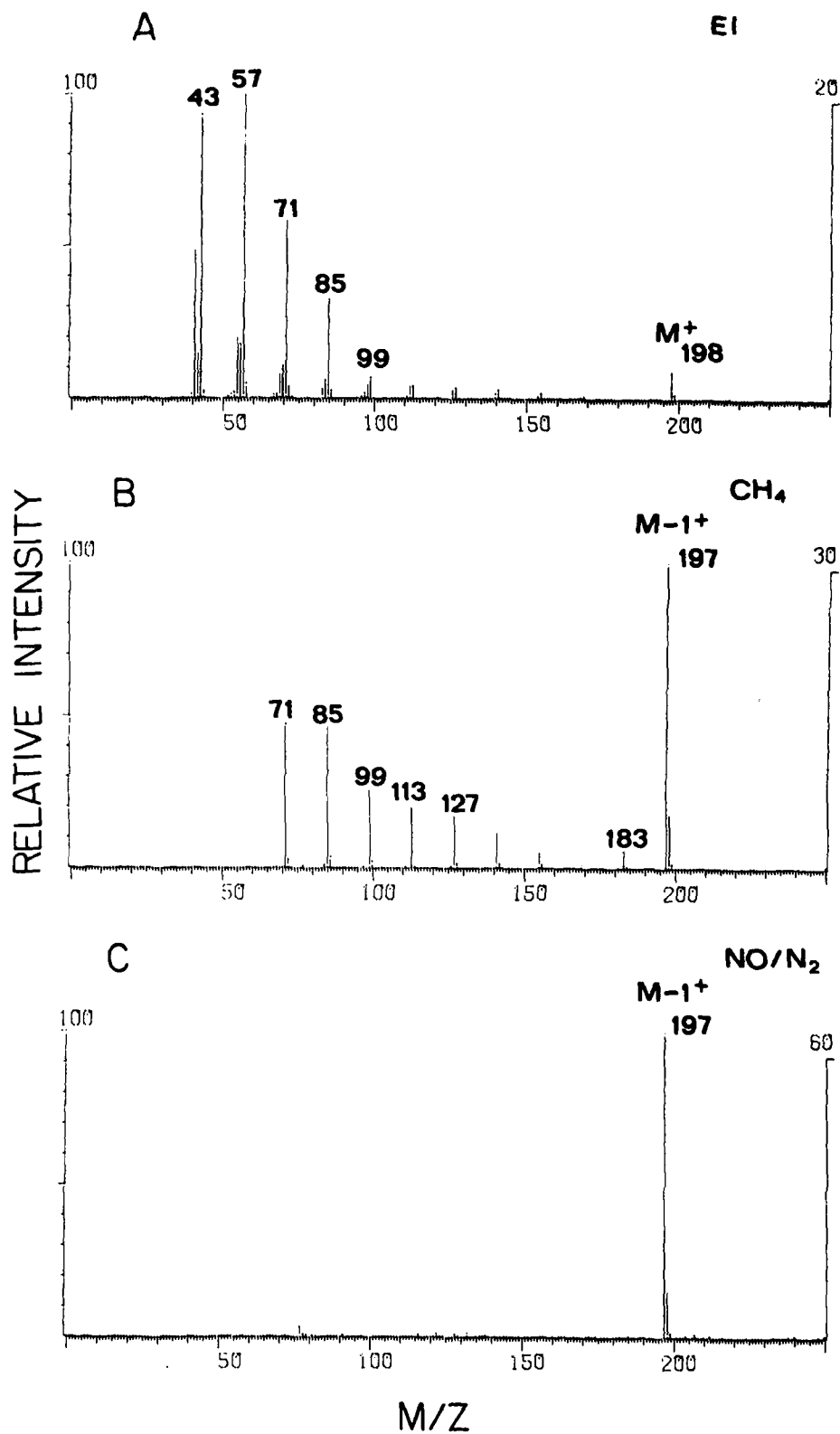


HOKE 4172G4Y	NUPRO SS-4H	NUPRO SS-4BMW

TABLE 1. Selected chemical ionization reagent gases.

Reactant Gas	Species	Proton Affinity Kcal/Mole		Behavior/Applications
Hydrogen	H <sub>3</sub> <sup>+</sup>	100		Strong Brönsted acid; proton transfer; hydride abstraction
Methane	CH <sub>5</sub> <sup>+</sup>	127		"Brönsted acid"
Water	H <sub>3</sub> O <sup>+</sup>	165		" "
Methanol	CH <sub>3</sub> OH <sub>2</sub> <sup>+</sup>	182		" "
Isobutane	t-C <sub>4</sub> H <sub>9</sub> <sup>+</sup>	195		" "
Ammonia	NH <sub>4</sub> <sup>+</sup>	207		Weak Brönsted acid; weak electrophile; polyfunctional structures
<div>-15-</div>				
Deuterium oxide	D <sub>3</sub> O <sup>+</sup>			Deuteration; active hydrogen exchange
Argon/water	Ar <sup>+</sup> /H <sub>3</sub> O <sup>+</sup>			Mixed charge exchange/chemical ionization
Nitric oxide	NO <sup>+</sup>			Electrophile; hydride abstractor; oxidant; functional group analysis
Vinyl methyl ether	CH <sub>3</sub> OCH=CH <sub>2</sub> <sup>+</sup>			Double bond positional isomers

FIGURE 5. Comparison of fragmentation patterns for n-tetradecane using  
(a) electron impact ionization, (b) methane-chemical ionization  
and (c) nitric oxide/nitrogen-chemical ionization.



Secondly, mixture components can be selectively ionized by matching the proton affinity or other chemical properties of the reactant gas to the mixture components of interest. Figure 6, for example, presents the results of two GC/CI-MS analyses, using methane and methanol, respectively, of a synthetic mixture containing over sixty low boiling compounds. These include aliphatic, olefinic, alicyclic, and aromatic hydrocarbons, alcohols, aldehydes, ketones, and amines. Using methane, all mixture components are ionized, although many of these overlap in the chromatogram. In contrast, when methanol is used as the reagent gas, less than one-third of the components, primarily ketones, amines and terpene alcohols (Table 2), are ionized and detected. The response to hydrocarbons, including aromatic hydrocarbons, is severely reduced or completely eliminated, effectively simplifying interpretation of the chromatogram. Thus, it is possible to screen out hydrocarbon contamination or background in the analysis of polar fractions by judicious choice of a selective reagent gas.

#### GC/MS Interface Design

Another aspect critical to the optimized performance of combined glass capillary GC and EI-MS or CI-MS is the GC/MS interface design. The connection between the chromatograph and the mass spectrometer may generally be one of three types: (1) the effusion or jet separator (RHYHAGE, 1964; WATSON and BIEMANN, 1964), (2) the open split connection (HENNEBERG et al., 1975a,b; SCHMID et al., 1979), or (3) the direct connection (GROB and JAEGGI, 1973; BLUM and RICHTER, 1975). We have chosen the direct connection method since this utilizes the entire sample and hence, optimizes sensitivity for trace analytical applications. A capillary interface (Figure 7) has been fabricated for the Finnigan 3200 GC/MS after the design of Blum and Richter (1975; 1977). The interface is a dual gas configuration in which the CI reactant gas flows coaxially around a glass capillary transfer line and mixes with the column effluent as it emerges



FIGURE 6. Comparison of two glass capillary GC/MS analyses of a synthetic mixture containing sixty-five low boiling compounds using (a) methane-chemical ionization, and (b) methanol-chemical ionization. Refer to Table 2 for identification of numbered peaks. Gas chromatographic conditions: Finnigan 9500 gas chromatograph; column, SE-52, 20 m x 0.31 mm; helium carrier, 0.5 atmosphere; temperature program, 20-200°C at 3°C/min. Mass spectrometer: Finnigan 3200; electron energy, 130 eV; methane source pressure, 950 microns (methanol, 500 microns); source temperature, 120°C.

# SELECTIVE IONIZATION OF COMPONENTS

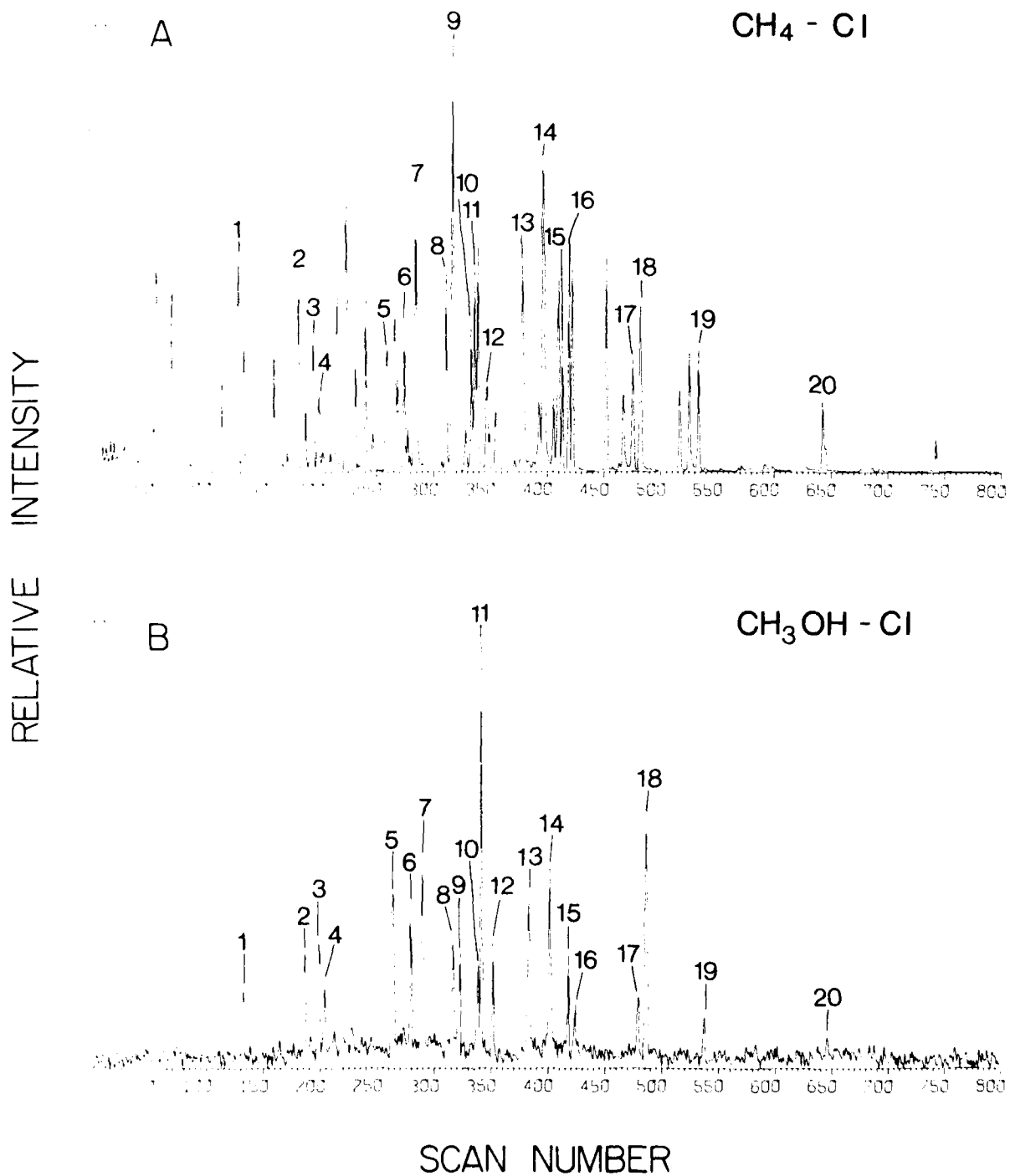
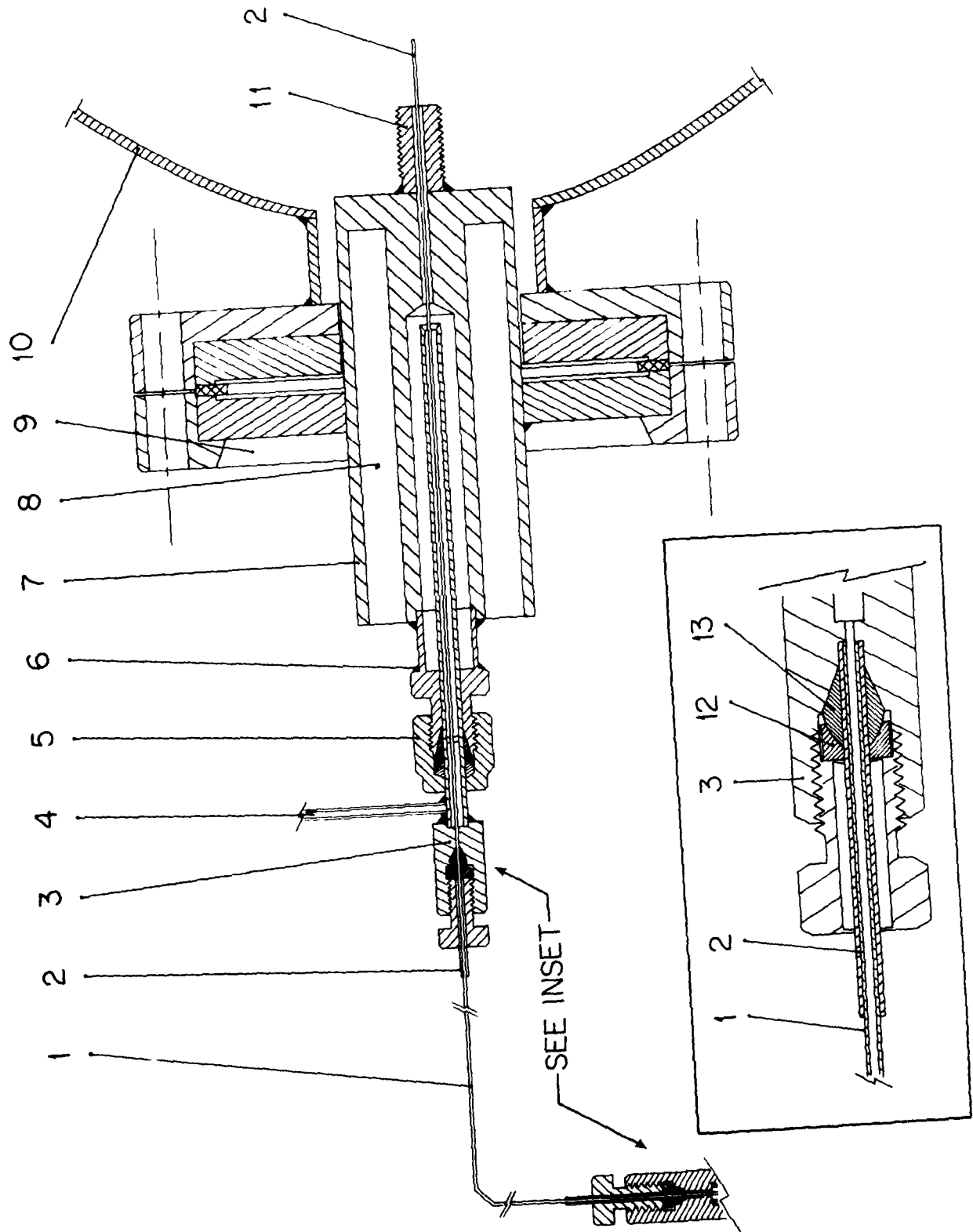


TABLE 2. Compound identities for numbered peaks in Figure 6.

Peak Number	Compound
1	Anisole
2	$\alpha$ -Methylstyrene
3	2-Octanone
4	2-Ethyl-2-hexenal
5	5-Nonanone
6	2-Nonanone
7	Linalool
8	Isopulegol
9	Unknown terpene alcohol
10	Terpinenol-4
11	2,6-Dimethylaniline
12	2-Decanone
13	$\beta$ -Citronellol
14	Geraniol
15	2-Undecanone
16	1-Methylnaphthalene
17	2-Dodecanone
18	Dicyclohexylamine
19	2-Tridecanone
20	2-Pentadecanone

FIGURE 7. Sectional view of dual gas coaxial interface for combined glass capillary gas chromatography-chemical ionization mass spectrometry (BLUM and RICHTER, 1975). (1) Pyrex glass capillary transfer line: 0.9 mm O.D.; 0.22 mm I.D., (2) Teflon shrink tubing, (3) Swagelok zero dead volume union, 1/16", (4) reagent gas entry line, 1/16" SS, (5) Swagelok butt weld male connector, 1/8" SS, (6) silver brazing, (7) heater block, SS, (8) cartridge heater cavity, (9) Varian Conflat rotatable flange, 2 3/4", (10) mass spectrometer vacuum manifold, (11) CI source nipple connection to ion source, (12) backup spacer, SS, (13) ferrule; 85%, Vespel, 15% graphite.



into the ionization chamber. This design has been tested for performance with glass capillary columns under both EI and CI conditions and has proven to have the following advantages:

(1) The glass capillary transfer line provides the chemically inactive surface required for the analysis of thermally sensitive or labile compounds. The surface can be coated with Carbowax 20 M using a modification of the Blomberg method (Blomberg, 1975) to give a film which is stable to 280°C and which shows minimal irreversible adsorption of polar compounds. Alternatively, the transfer line can be deactivated using vapor phase silanization (WELSCH, 1977) when higher operating temperatures (< 350°C) are required.

(2) Little or no degradation in separation performance is observable since the "straight-through" capillary connection minimizes the dead space associated with valving and coupling connectors.

(3) The reactant gas can be selected independently from the choice of carrier gas, i.e. the properties of the reactant gas (viscosity, corrosiveness, etc.) need not be considered when optimizing the chromatographic conditions. This also facilitates direct comparison of data produced from GC/EI-MS and GC/CI-MS analyses since flow conditions remain identical.

The performance of the coaxial interface is illustrated in Figure 8, which shows the reconstructed gas chromatogram (methane-chemical ionization) of another synthetic mixture containing a variety of compound classes (Table 3). Chromatographic resolution is not significantly degraded due to the interface and individual components are seen to elute as sharp, symmetrical peaks with minimal tailing.

An interface of similar design using the direct glass capillary connection, but without the coaxial gas feature has been constructed for the Finnigan 1015 GC/MS and is used solely in the EI ionization mode.

FIGURE 8. Computer-reconstructed gas chromatogram of a synthetic mixture illustrating the performance attainable with a coaxial dual gas chemical ionization interface. Peak identifications are given in Table 3. Gas chromatographic conditions: Finnigan 9500 gas chromatograph; column, Emulphor ON-870, 50 m x 0.35 mm; helium carrier, 1.5 atmosphere; temperature program, 50-200°C at 2°C/min. Mass spectrometer: Finnigan 3200; electron energy, 130 eV; methane source pressure, 950 microns, source temperature, 120°C. Sample mixture obtained courtesy of W. Blum, Ciba-Geigy AG, Basel, Switzerland.



SYNTHETIC MIXTURE CI-METHANE

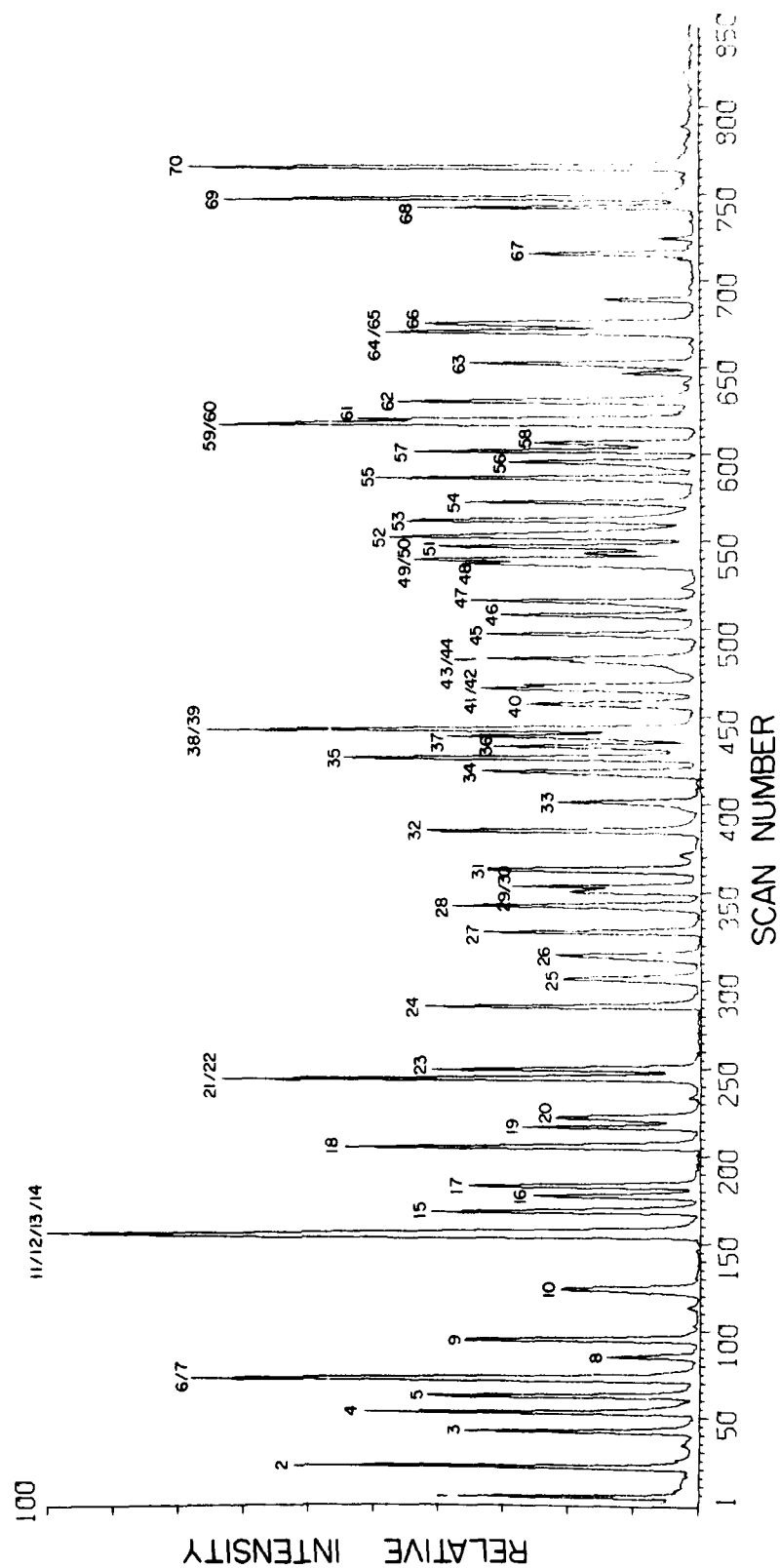


TABLE 3. Synthetic mixture component identities  
(refer to Figure 8).

Peak Number	Compound Identity	Peak Number	Compound Identity
1	n-Decane	36	n-Heptylbenzene
2	Ethylbenzene	37	Phenylcyclohexane
3	n-Undecane	38	2,6-Dichlorostyrene
4	Chlorobenzene	39	Diethyl succinate
5	n-Propylbenzene	40	1,5-Dibromopentane
6	4-Ethyltoluene	41	Naphthalene
7	1,8-Cineole	42	2-(n-Heptyl)-1-nonene
8	tert.-Butylbenzene	43	n-Hexadecane
9	sec.-Butylbenzene	44	2-Methylacetophenone
10	n-Dodecane	45	4-Methylacetophenone
11	2-Methyl-3-phenyl-1-propene	46	4-Isopropylbenzaldehyde
12	Anisole	47	n-Octylbenzene
13	n-Butylbenzene	48	1,6-Dibromohexane
14	Bromobenzene	49	Nerol
15	6-Methyl-5-hepten-2-one	50	2-Bromobenzaldehyde
16	tert-Pentylbenzene	51	2,6-Dimethylaniline
17	sec.-Pentylbenzene	52	2-Chlorophenol
18	Cyclohexyl methyl ketone	53	Benzyl alcohol
19	1-Phenyl-2-butene	54	1-Methylnaphthalene
20	n-Tridecane	55	1-Phenyl-1-heptyne
21	1,4-Diisopropylbenzene	56	n-Nonylbenzene
22	1,4-Dichlorobenzene	57	2-Chloroaniline
23	n-Pentylbenzene	58	Diethyl adipate
24	Benzofuran	59	2-Ethyl-naphthalene
25	2-(n-Hexyl)-1-octene	60	2-Methoxybenzaldehyde
26	n-Tetradecane	61	2,6-Dichloroaniline
27	N,N-Dimethylaniline	62	2-Bromophenol
28	n-Hexylbenzene	63	1,3-Dimethylnaphthalene
29	1,4-Dibromobutane	64	1,4-Dimethylnaphthalene
30	4-Bromochlorobenzene	65	n-Decylbenzene
31	Diethyl malonate	66	1,2-Dimethylnaphthalene
32	Methyl benzoate	67	1,8-Dimethylnaphthalene
33	n-Pentadecane	68	4-Chloroaniline
34	(+)-Pulegone	69	3-Chloroaniline
35	Ethyl benzoate	70	2-Aminoacetophenone

### Applications in Marine Chemistry

Recent applications of this improved instrumentation include the identification of volatile organic compounds in seawater, the distributions of various lipid class compounds in marine phytoplankton, sediments, and particulate matter, and the behavior of anthropogenic pollutants in natural and artificial marine ecosystems.

A previously uninvestigated fraction of the organic matter in seawater, volatile organic compounds, ranging from low to medium polarity and falling within the approximate boiling range between n-heptane and n-octadecane, may be expected to include a diversity of compound classes and may be useful as tracers or indicators for important biological and chemical processes. A large number of low boiling organic compounds (Figures 9 & 10) stripped from seawater using a recirculating stripper (GROB and ZÜRCHER, 1976) have been identified using glass capillary GC and GC/MS (SCHWARZENBACH et al., 1978; GSCHWEND, 1979). Total recoveries for volatiles ranged from 0.2-1.0 µg/kg volatile organic carbon/kg, with individual compounds being present at concentration levels of 1-10 ng/kg (Table 4). At these low concentration levels, EI spectra frequently were not interpretable and chemical ionization techniques became the key to compound identification. The CI-methane spectra were found to provide sufficiently intense quasi-molecular ions and, in many cases, enough structural information to characterize specific components down to concentrations of 1 ng/kg seawater.

In addition to improving detection limits, CI-methane spectra provided a more accurate representation of isomer distributions within compound classes. Since isomeric compounds within a given compound class generally have similar proton affinities, the M+1 (or M-1) mass chromatograms directly indicate relative amounts of each isomer present in the sample. Mesitylene (C<sub>3</sub>-benzene),

FIGURE 9. Volatile organic compounds in Massachusetts coastal waters: (a) Buzzards Bay surface water, (b) Vineyard Sound surface water during spring phytoplankton bloom, (c) Vineyard Sound surface water after fuel oil spill in nearby Buzzards Bay (SCHWARZENBACH et al., 1978; GSCHWEND, 1979). See Table 4 for identification of numbered peaks.

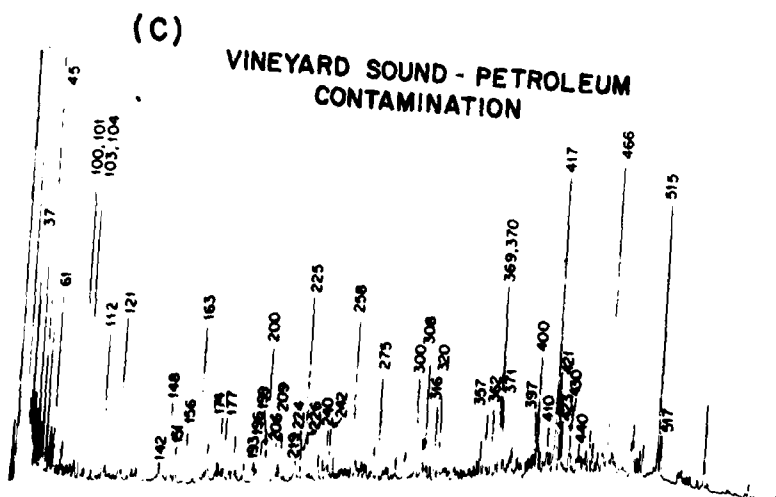
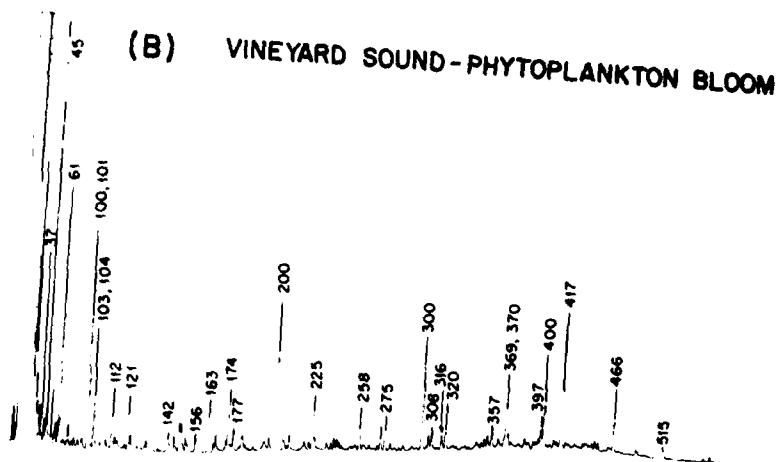
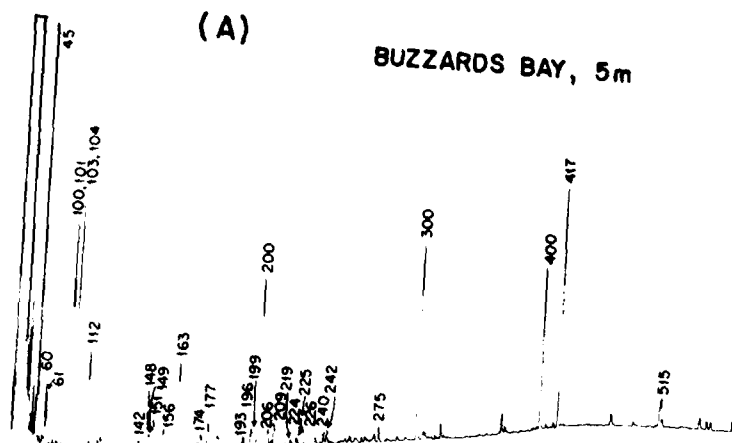
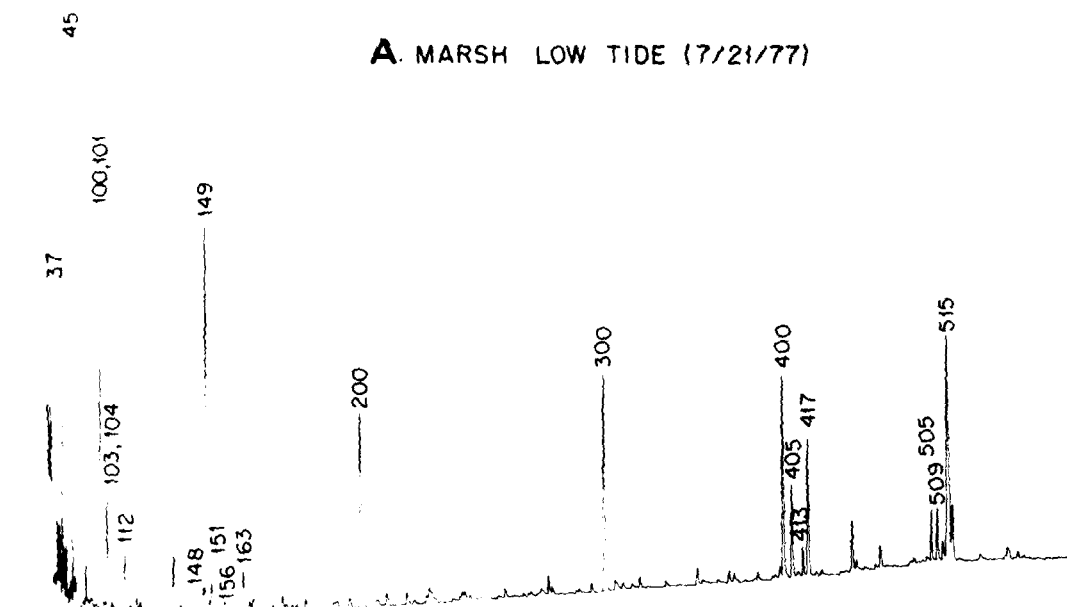


FIGURE 10. Comparison of volatile organic compounds in salt marsh water sampled during (a) low tide and (b) high tide (SCHWARZENBACH et al., 1978). See Table 4 for identification of numbered peaks.

A. MARSH LOW TIDE (7/21/77)



B. MARSH HIGH TIDE (7/19/77)

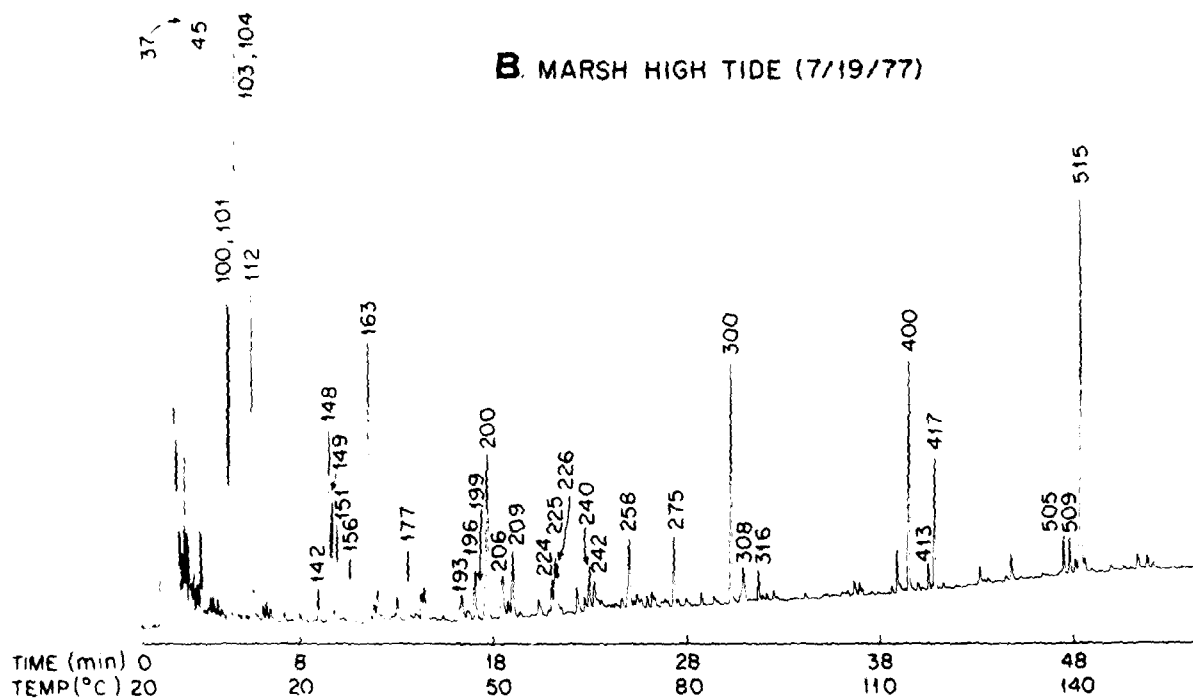




TABLE 4. Structures and concentration ranges of volatile organic compounds found in coastal seawater as shown in Figures 9 & 10 (Schwarzenbach et al., 1978).

Peak Number	Structure	Concentration (ng/kg)		Peak Number	Structure	Concentration (ng/kg)	
		Vineyard Sound	Salt Marsh			Vineyard Sound	Salt Marsh
37	Dimethyldisulfide			240	C <sub>10</sub> H <sub>12</sub>	2-10	tr-4
45	Toluene	> 10	> 10	242	C <sub>4</sub> -Benzene	2-10	tr-4
60	Tetrachloroethylene	5	5	258	Naphthalene	5-40	tr-10
61	n-Hexanal		tr-10	275	n-Decanal	5-50	tr-20
100	1-Chloro-n-hexane *	5-100	(10)	300	1-Chloro-n-decane *	(10)	(10)
101	Ethylbenzene	5-25	2-20	309	2-Methylnaphthalene	2-25	tr-5
103	1,3-Dimethylbenzene	15-50	6-40	316	1-Methylnaphthalene	1-20	tr-5
104	1,4-Dimethylbenzene			320	n-Tridecane	0-5	1
109	Bromoform			357	2-Ethyl-naphthalene	0-15	--
112	1,2-Dimethylbenzene	5-25	2-20	362	2,6-Dimethylnaphthalene	0-20	--
121	n-Heptanal	5-40	tr-10	369	n-Tetradecane	0-10	tr
142	n-Propylbenzene	tr-3	0-2	370	C <sub>2</sub> -Naphthalene	0-20	tr
148	C <sub>3</sub> -Benzene	4-20	1-12	371	C <sub>2</sub> -Naphthalene	tr-20	--
149	Dimethyltrisulfide			397	Acenaphthalene	tr-15	--
151	1,3,5-Trimethylbenzene	3-15	1-8	400	1-Chloro-n-dodecane *	(10)	(10)
156	C <sub>3</sub> -Benzene	2-10	1-6	405	C <sub>15</sub> H <sub>30</sub>	--	tr-5
163	C <sub>3</sub> -Benzene	5-25	2-15	410	C <sub>3</sub> -Naphthalene	tr-10	--
174	n-Octanal	5-40	tr-10	413	C <sub>15</sub> H <sub>30</sub>	--	1-3
177	C <sub>3</sub> -Benzene	2-10	1-6	417	n-Pentadecane	5-100	5-15
193	C <sub>4</sub> -Benzene	1-5	tr-2	421	C <sub>3</sub> -Naphthalene	tr-10	--
196	C <sub>4</sub> -Benzene	2-10	tr-4	423	C <sub>3</sub> -Naphthalene	tr-10	--
199	C <sub>4</sub> -Benzene	1-5	tr-2	430	C <sub>3</sub> -Naphthalene	tr-10	--
200	1-Chloro-n-octane *	(10)	(10)	440	C <sub>3</sub> -Naphthalene	tr-10	--
206	C <sub>4</sub> -Benzene	2-10	tr-4	466	n-Hexadecane	1-20	1-3
209	C <sub>4</sub> -Benzene	2-10	tr-4	505	C <sub>17</sub> H <sub>34</sub>	--	1-12
219	C <sub>4</sub> -Benzene	2-5	tr-2	509	C <sub>17</sub> H <sub>34</sub>	--	1-3
224	C <sub>4</sub> -Benzene	2-5	tr-3	515	n-Heptadecane	1-30	5-30
225	n-Nonanal	5-70	tr-20	517	Pristane	tr-5	--
226	C <sub>4</sub> -Benzene	2-10	tr-4				

\* Internal standard.

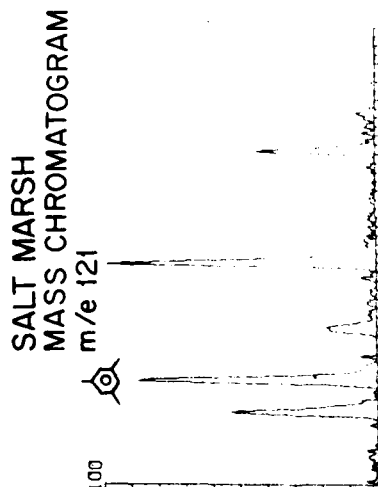
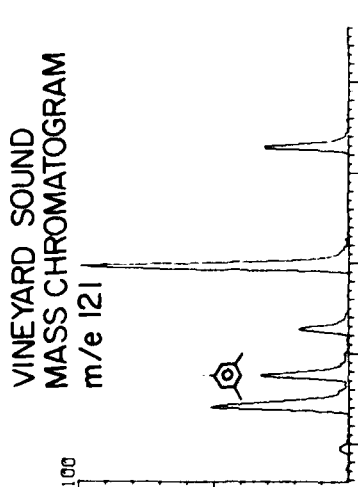
for example, frequently was found to be enriched in tidal marsh samples relative to Vineyard Sound waters (Figure 11a). In contrast, the  $C_3$ -naphthalene distributions for samples of Vineyard Sound water were strikingly similar to that observed for a No. 2 fuel oil (Figure 11b). This suggests that combined glass capillary GC/CI-MS will be an excellent tool for studies of natural and anthropogenic sources of organic compounds, as well as specific transformation and removal processes for individual isomers.

In another application, fatty acid distributions have been examined quantitatively in marine algal cells (SCHWARZENBACH and FISHER, 1978), and semi-quantitatively in marine sediments (FREW et al., unpublished data) using iso-butane as a reactant gas. Chemical ionization iso-butane spectra of free fatty acids consist essentially of a single ion (the protonated molecular ion) along with a low intensity fragment ( $M+1-18$ ) resulting from dehydration of the  $M+1$  ion (Figure 12). Spectra of the fatty acid methyl esters contain  $M+1$  ions only. The simplicity of the iso-butane spectrum therefore allows rapid measurements of the molecular weight distributions of fatty acids in complex mixtures. Figure 13 presents direct insertion probe mass spectra of the fatty acids which were observed in the marine diatom, Thalassiosira pseudonana, in culture (SCHWARZENBACH and FISHER, 1978). Using this technique, compositional changes in the diatom fatty acids during different phases of growth could be clearly delineated and were used to monitor physiological response to environmental factors (FISHER and SCHWARZENBACH, 1978).

The fatty acid mixtures observed in marine sediments are considerably more complex. Figure 14 shows a capillary gas chromatogram of fatty acids isolated from a sediment on the northeastern U.S. continental slope (Deep Ocean Station 1) using saponification-methylation extraction and thin layer chromatography separation of the methyl esters. The extract contained approximately two hundred

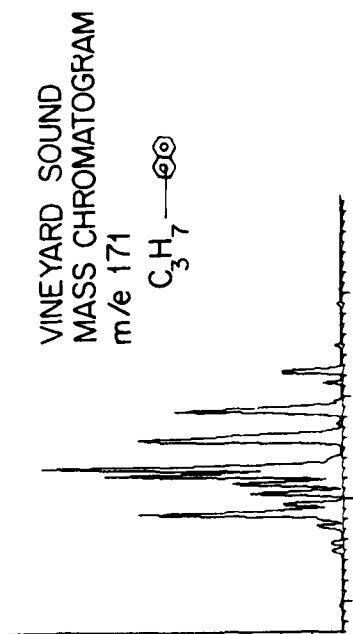
FIGURE 11. Mass chromatograms comparing (a) the alkyl benzene isomer distributions in Vineyard Sound surface waters and salt marsh water, and (b) the alkyl naphthalene isomer distributions in Vineyard Sound surface waters and a No. 2 fuel oil sample (SCHWARZENBACH et al., 1978).

(A)



SCAN

(B)



SCAN

RELATIVE INTENSITY

RELATIVE INTENSITY

FIGURE 12. Comparison of mass spectra of stearic acid ( $C_{18:0}$  fatty acid) using (a) electron impact ionization, and (b) iso-butane chemical ionization (SCHWARZENBACH and FISHER, 1978).

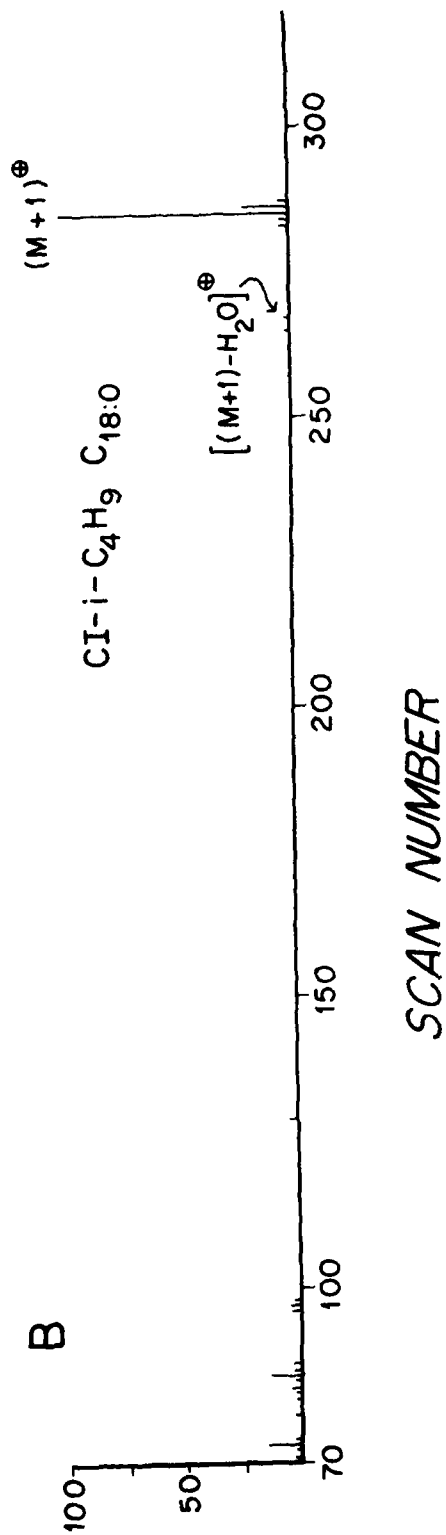
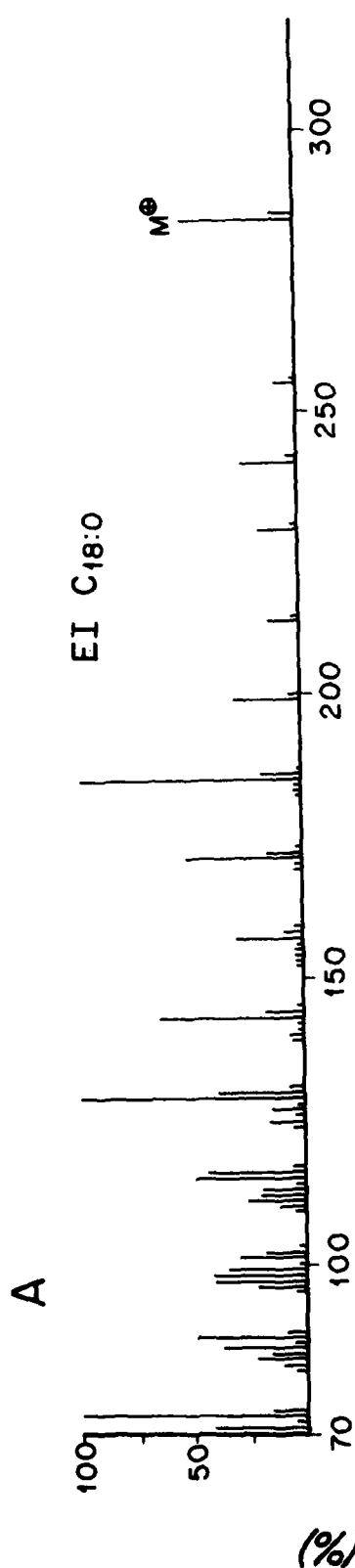
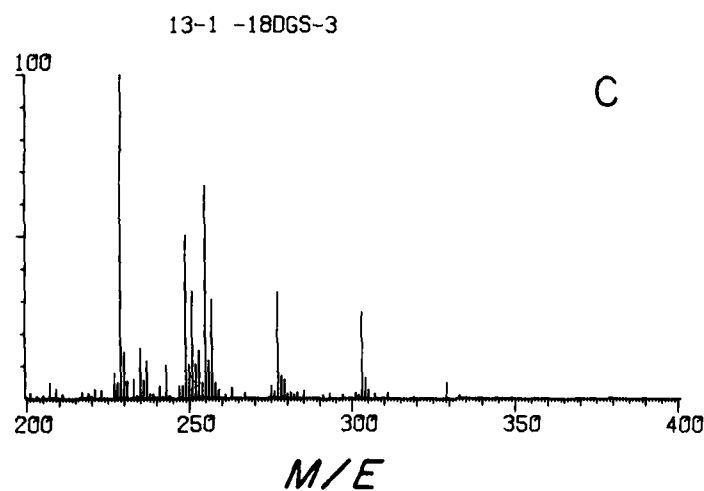
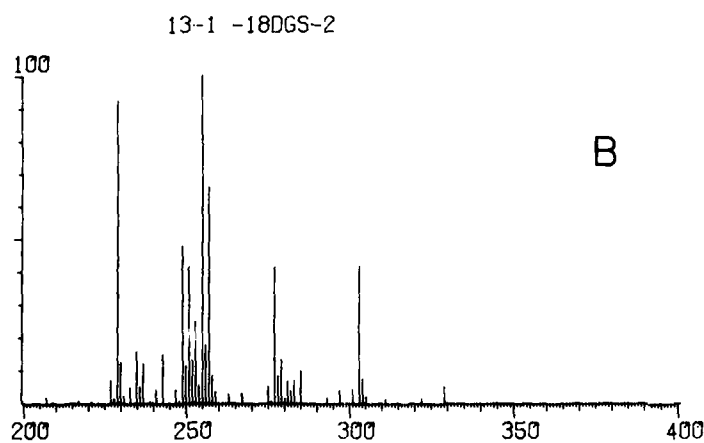
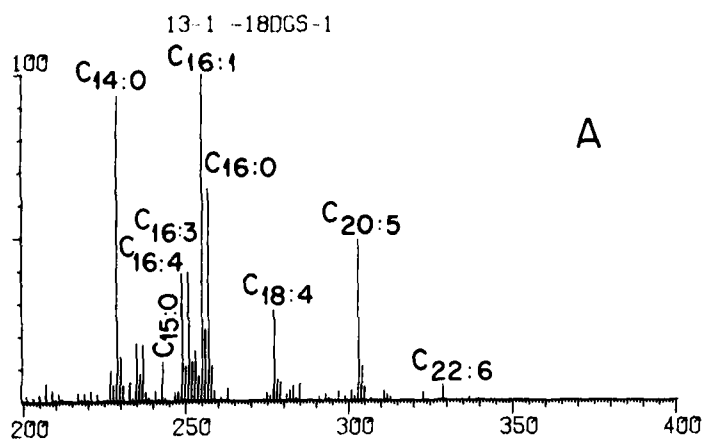


FIGURE 13. Iso-butane chemical ionization "total mass spectra" showing compositional changes of the fatty acids in the marine diatom Thalassiosira pseudonanna during different phases of growth: (a) early exponential, (b) late exponential, and (c) stationary (SCHWARZENBACH and FISHER, 1978).

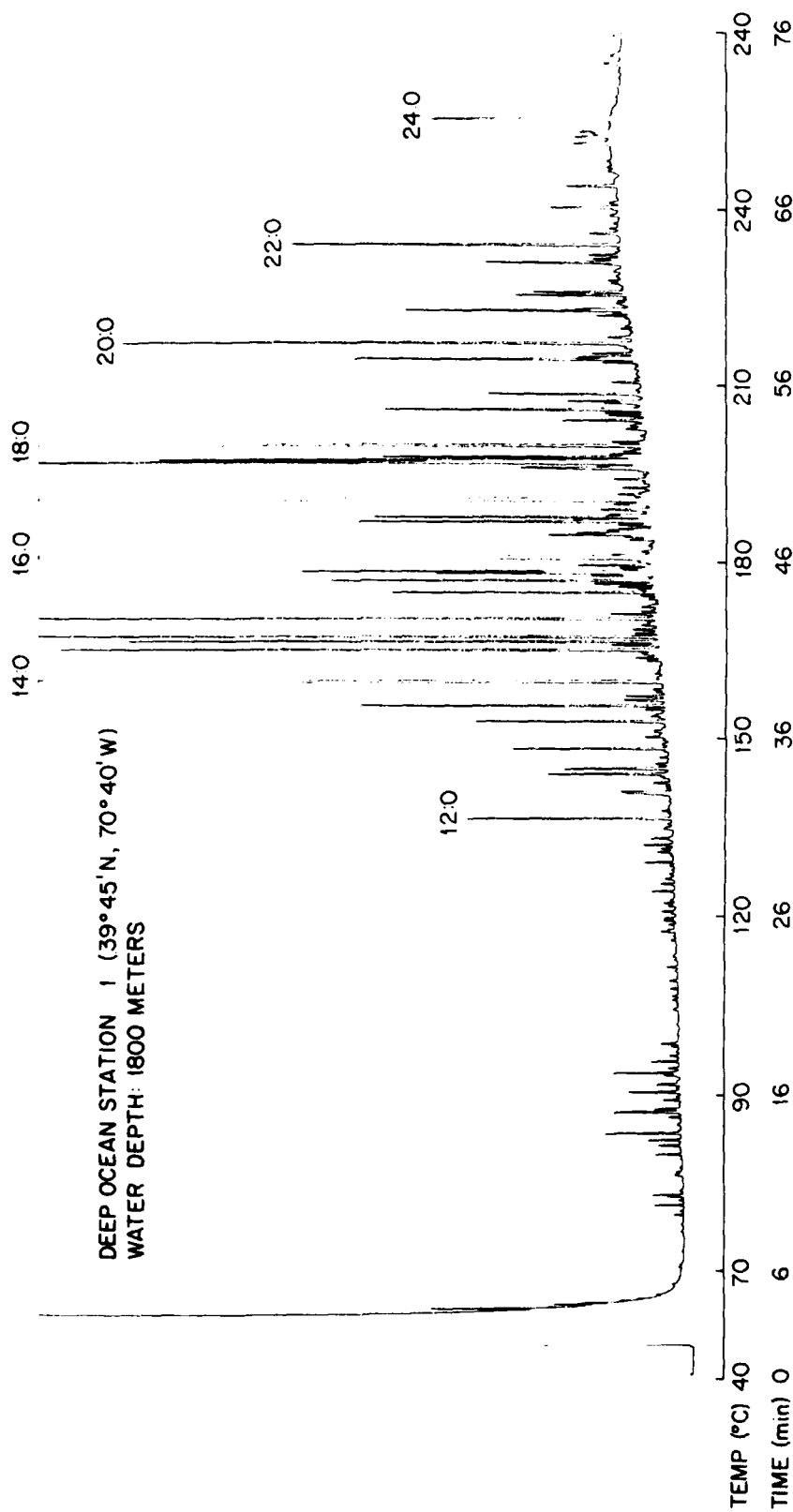




RELATIVE INTENSITY

$m/e$

FIGURE 14. Glass capillary chromatogram of fatty acids (methylated derivatives) isolated from a sediment core (2-6 cm section) collected on the northeastern U.S. continental slope at 39°45'N, 70°40'W. Separation performed on a Carlo Erba 2150 equipped with an SE-52 barium carbonate type column, 25 m x 0.31 mm; helium carrier, 0.6 atmospheres; temperature program, 40-240°C at 3°C/min.

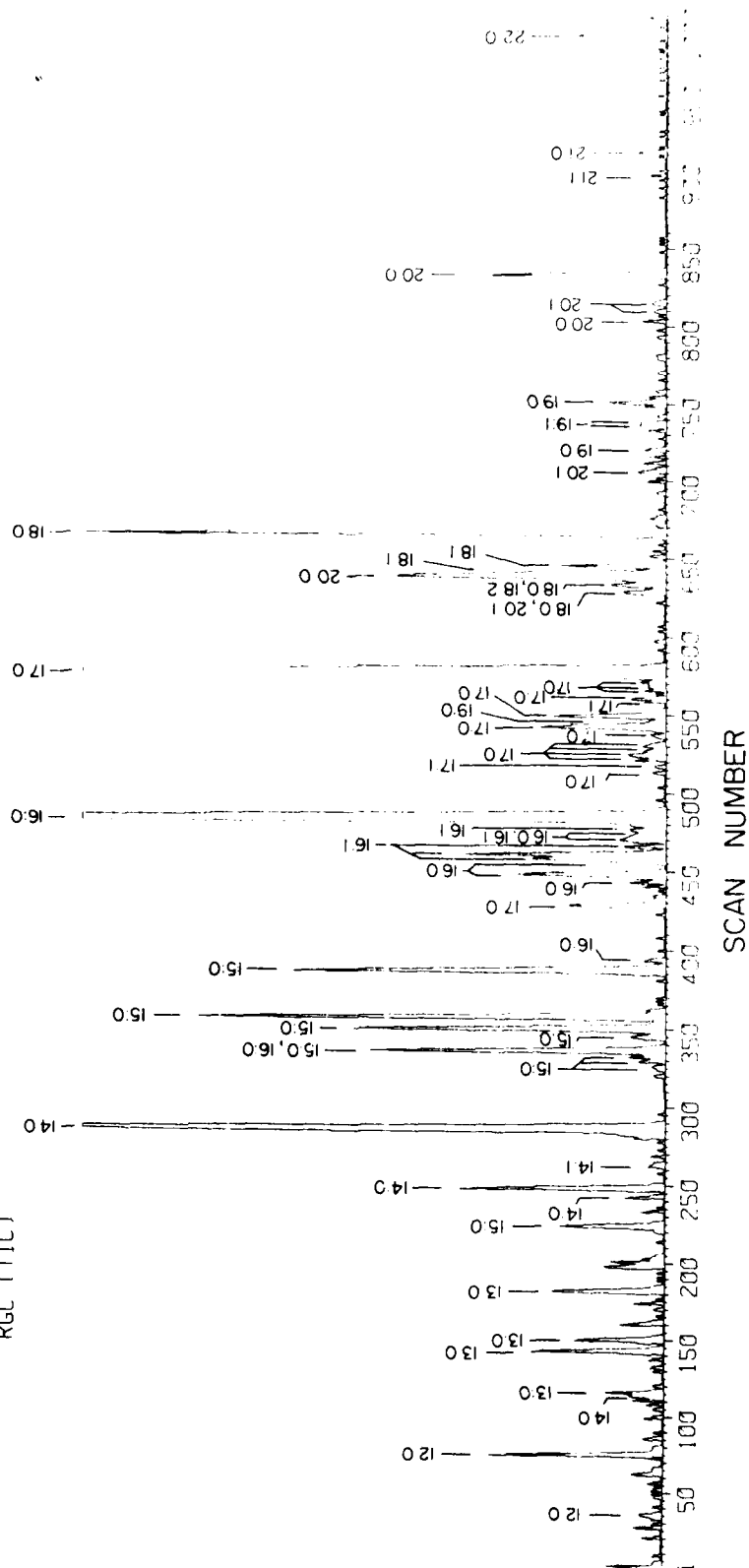


resolved or partially resolved components, many occurring at levels less than one percent relative to the most abundant component. Results of glass capillary GC/EI-MS analyses were similarly complex. Overlapping fragments and the absence of intense molecular ions prevented identification of many minor and trace components, while the presence of non-fatty acid components further complicated the EI analysis. Using iso-butane chemical ionization, however, about seventy acids in the twelve to twenty-two carbon range were partially characterized. These are indicated according to carbon number and degree of unsaturation in the CI-iso-butane trace of Figure 15. Cis and trans isomers of monoenoic acids could be separated without difficulty and overall isomer distributions were easily assessed from the appropriate M+1 mass chromatograms. The detailed information regarding trace isomer abundances suggests that the chemical ionization technique has considerable potential for further studies of fatty acid geochemistry in different types of marine environments.

The quality of information obtained in various GC/EI-MS applications has also been significantly enhanced using glass capillary columns and the interfacing technique described earlier. Steroidal compounds including stenols, stanols, steroid ketones, sterenes and steranes have been examined in a number of seawater, sediment, and particulate matter samples from different geochemical environments using glass capillary GC/EI-MS (GAGOSIAN, 1976; LEE et al., 1977; GAGOSIAN and FARRINGTON, 1978; GAGOSIAN and HEINZER, 1979; GAGOSIAN et al., 1979a,b; GAGOSIAN and NIGRELLI, 1979; GAGOSIAN and SMITH, 1979; LEE et al., 1979; LEE et al., 1980). The high temperature apolar columns prepared by vapor phase silanization are especially suitable for this application because of their thermal stability and low bleed rate. Stanols have been partially or completely separated from their stenol counterparts on such columns, as shown for the

FIGURE 15. Computer reconstructed gas chromatogram for selective iso-butane chemical ionization analysis of methylated fatty acids isolated from a sediment core at Deep Ocean Station 1 (Figure 14). Fatty acid structures designated according to carbon number and degree of unsaturation, e.g.  $C_{18:1}$  = 18 carbon atoms and 1 double bond.

Gas chromatographic conditions: Finnigan 9500 gas chromatograph; column, SE-52, 20 m x 0.31 mm; helium carrier, 0.8 atmosphere; temperature program, 70-250°C at 4°C/min. Mass spectrometer: Finnigan 3200; electron energy, 130 eV; iso-butane source pressure, 750 microns; source temperature, 120°C.



standard mixture in Figure 16. The sterol composition of a marine particulate matter sample collected in a sediment trap in the equatorial Atlantic (PARFLUX E site) is shown in the total ion chromatogram in Figure 17. Extracted ion chromatograms for prominent sterol ion fragments are shown in Figures 18-19 and the corresponding mass spectra for three representative sterols in the sediment trap material are presented in Figures 20-22.

Polychlorinated biphenyl (PCB) compounds have been monitored in benthic chamber experiments in Buzzards Bay, Massachusetts (FARRINGTON et al., 1979). Infaunal organisms such as polychaete worms were shown by mass chromatography to concentrate polychlorinated biphenyls from sediments contaminated at low levels (Figure 23).

Other applications include studies of transport and degradation processes which determine the fate of petroleum hydrocarbons introduced to marine ecosystems. In a series of experiments at the Marine Ecosystem Research Laboratory, University of Rhode Island, the effects of low level chronic oil contamination in an artificial mesoscale marine ecosystem were monitored using high resolution GC/EI-MS (GEARING et al., 1979; FREW et al., 1979). Water dispersions of No. 2 fuel oil were periodically added to large tanks containing Narragansett Bay water/silt-clay sediment systems which supported natural planktonic and benthic communities. Specific low level aromatic hydrocarbons from the oil were followed quantitatively and distinguished from other sources by means of their isomer and homolog distribution patterns. The total ion chromatogram for a total pentane extract of the initial fuel oil-water dispersion (Figure 24) reflects an extremely complex hydrocarbon mixture. The naphthalene and phenanthrene components of this mixture are shown in Figure 25. Figure 26 shows the distribution of these compounds in the tank water during a time series experiment. Rapid compositional changes including losses of lower molecular

FIGURE 16. Computer reconstructed gas chromatogram of a standard stanol/stenol mixture (acetylated). See Table 5 for identification of numbered peaks. Gas chromatographic conditions: Varian 1400 gas chromatograph; column, SE-52, 20 m x 0.32 mm (high temperature); injector, 290°C; interface, 300°C; helium carrier, 0.5 atmosphere; temperature program, 150-280°C at 2°C/min. Mass spectrometer: Finnigan 1015; electron impact ionization, 70 eV.



FILE NMFO02 DA ACQUISITION TABLE NAME DEFACQ DATE 12/6/1979  
TITLE STANOL/STENOL STANDARD ACETYLATED 1.0 UL

BASELINE SCAN 1102

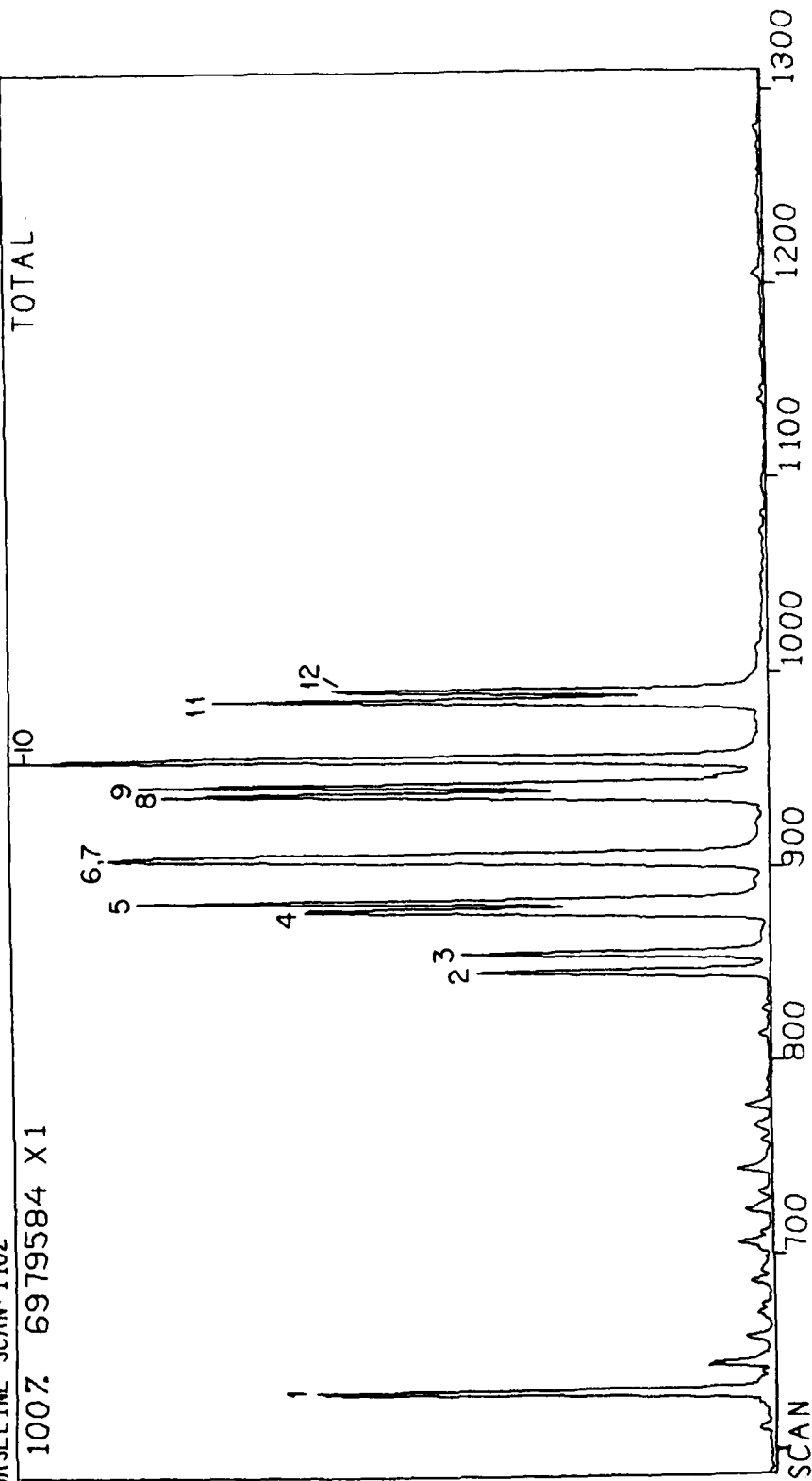
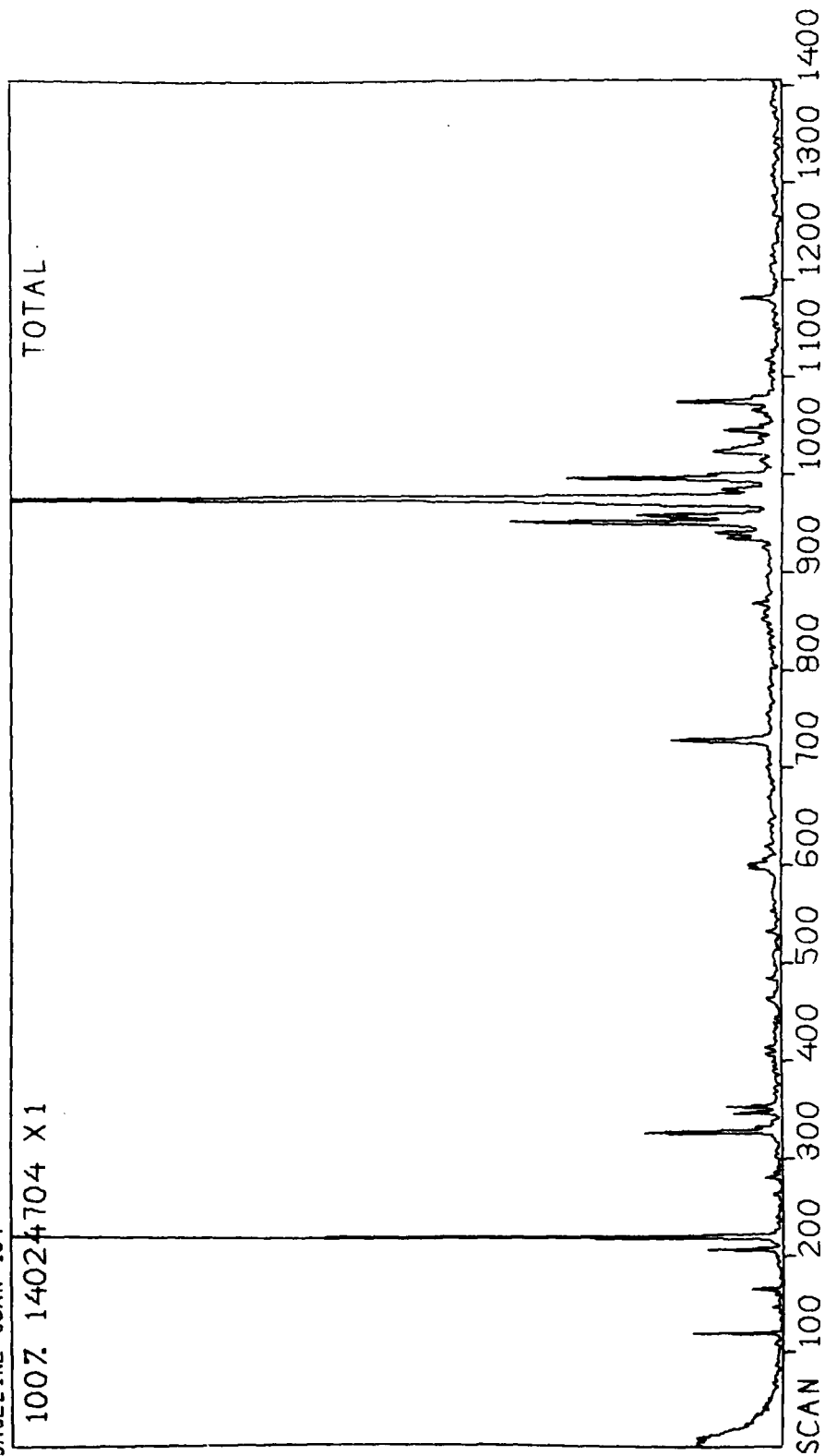


TABLE 5. Composition of standard stanol/stenol mixture shown in Figure 16.

Peak Number	Compound Identification	Concentration (ng/ $\mu$ l)
1	Cholestane (internal standard)	10.9
2	22(Z)-Dehydrocholesterylacetate	8.5
3	22(E)-Dehydrocholesterylacetate	10.0
4	Cholesterylacetate	14.7
5	Cholestanylacetate	15.9
6	Brassicasterylacetate	19.2
7	$\Delta^7$ -Cholesterylacetate	16.0
8	Campesterylacetate	18.2
9	Campestanylacetate	18.5
10	Stigmasterylacetate	20.5
11	$\beta$ -Sitosterylacetate	16.2
12	Stigmastanylacetate	14.0

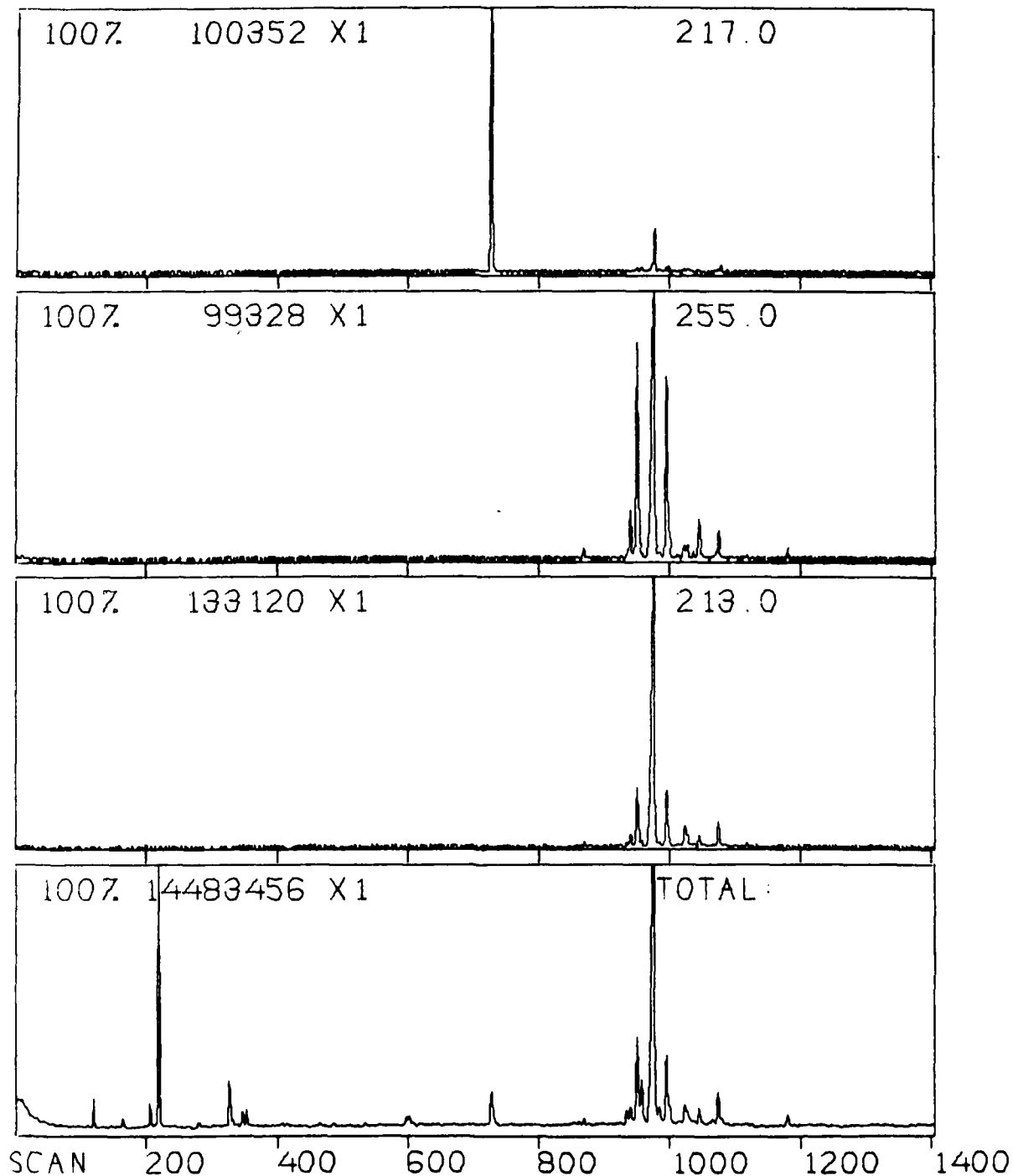
FIGURE 17. Sterol fraction isolated as acetates from organic material collected in a sediment trap at the PARFLUX E site in the equatorial Atlantic. Sediment trap depth: 388 meters. Analysis conditions as given in Figure 16.

FILE NMFO01 DA ACQUISITION TABLE NAME TSTIFS DATE 1/23/1979  
TITLE PARFLUX SEDIMENT TRAP EG 388 METERS STEROLS ACETYLATED  
BASELINE SCAN 137



FIGURES 18 & 19. Selected mass chromatograms for characteristic acetylated stenol ions in the PARFLUX E sediment trap sample of Figure 17. M/e 217 also shown to indicate retention time of cholestane used as internal standard.

NMF001 DA ACQUISITION TABLE NAME TSTIFS DATE 7/23/1979  
TITLE PARFLUX SEDIMENT TRAP E6 388 METERS STEROLS ACETYLATED



FILE: NMF001.DA ACQUISITION TABLE NAME: TSTIFS DATE: 1/23/1979  
TITLE: PARFLUX SEDIMENT TRAP E6 388 METERS STEROLS ACETYLATED

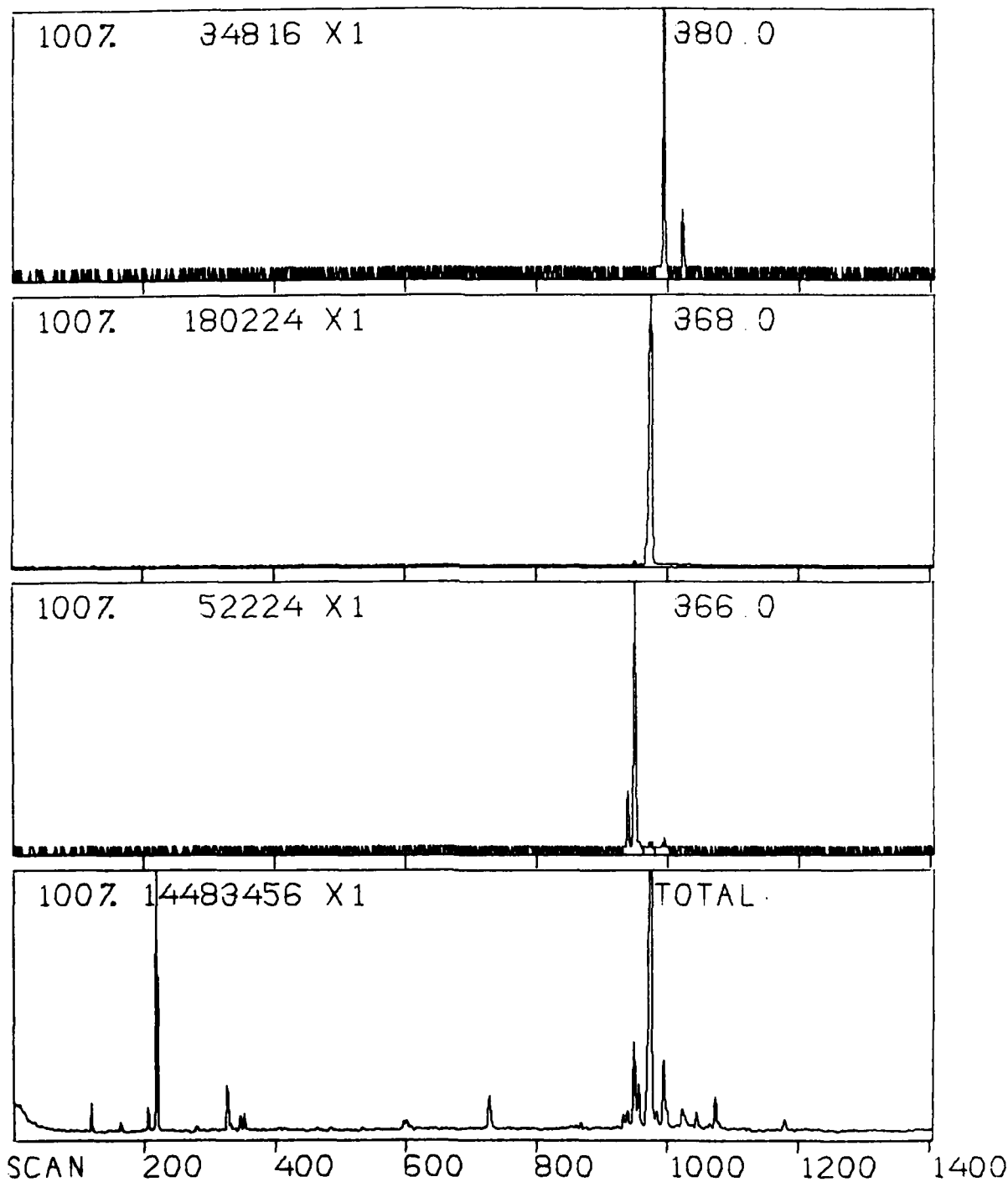




FIGURE 20. Mass spectrum of acetyl derivative of cholesta-5,22(E)-dien-3 $\beta$ -ol identified in PARFLUX E sediment trap material from 388 meter depth.

NMF001 DA SCAN 950 SIGMA 17 RT 44.34 BACKGD 943X100 100% 252928

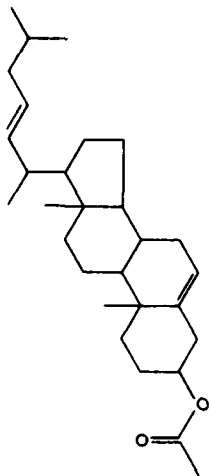
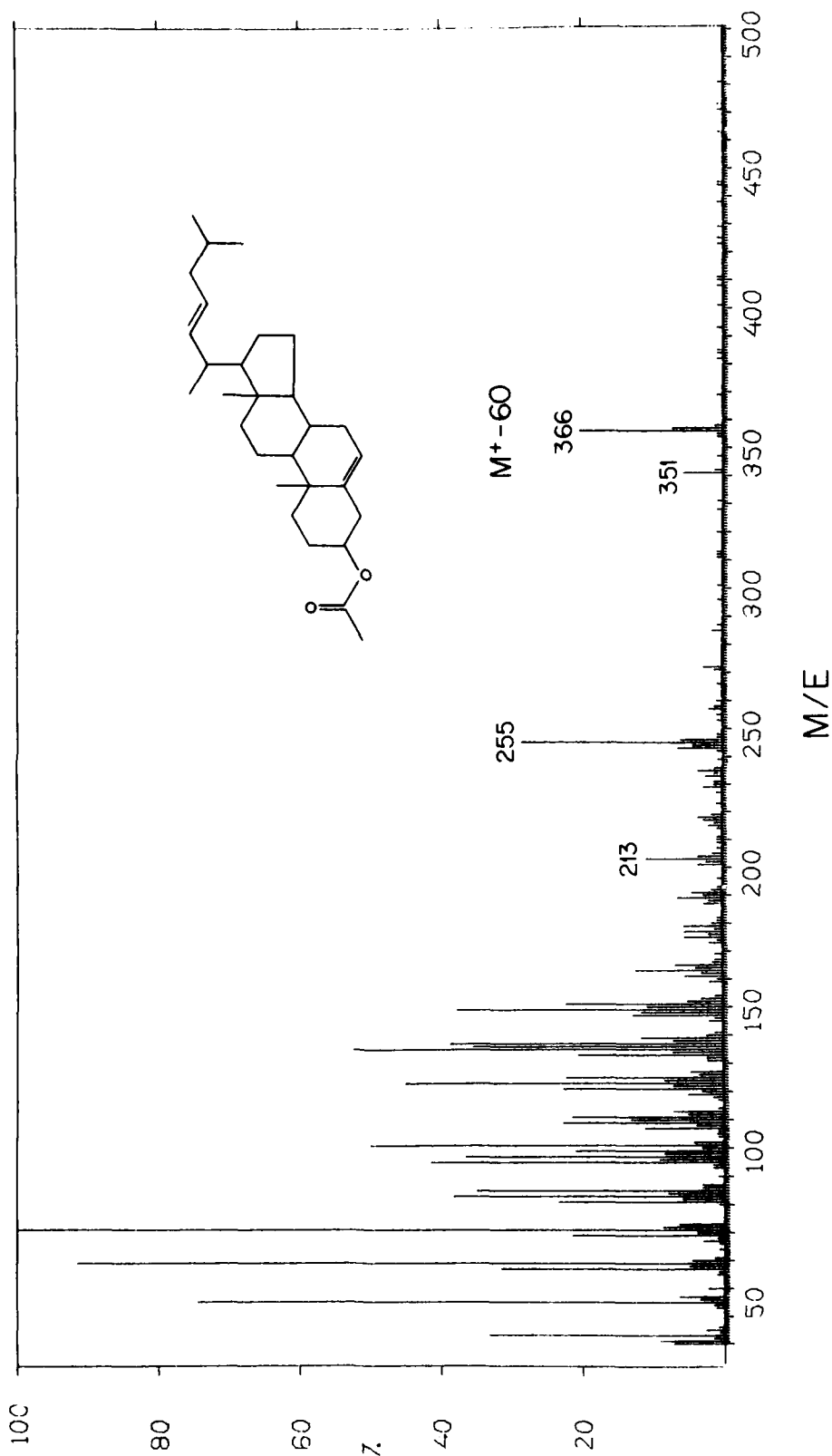


FIGURE 21. Mass spectrum of acetyl derivative of cholest-5-en-3 $\beta$ -ol (cholesterol) identified in PARFLUX E sediment trap material from 388 meter depth.

NMFO01 DA SCAN 972 SIGMA 18 RT 45.36 BACKGD 963X100 100% 423936

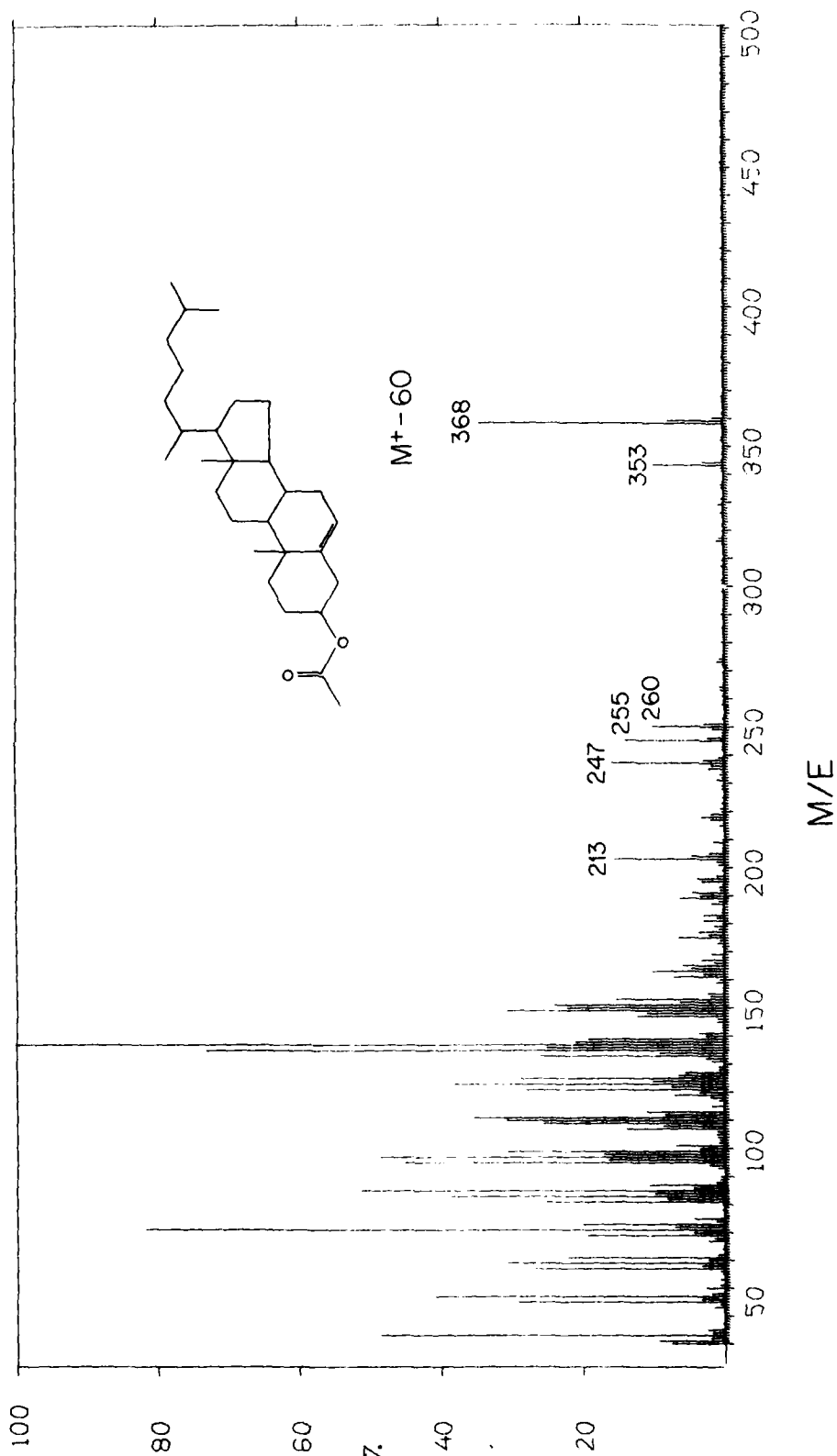


FIGURE 22. Mass spectrum of acetyl derivative of 24-methylcholesta-5,22-dien-3 $\beta$ -ol (brassicasterol) identified in PARFLUX E sediment trap material from 388 meter depth.

NMF001 DA SCAN 996 SIGMA 14 RT 46 43 BACKGD 988X100 100% 286720

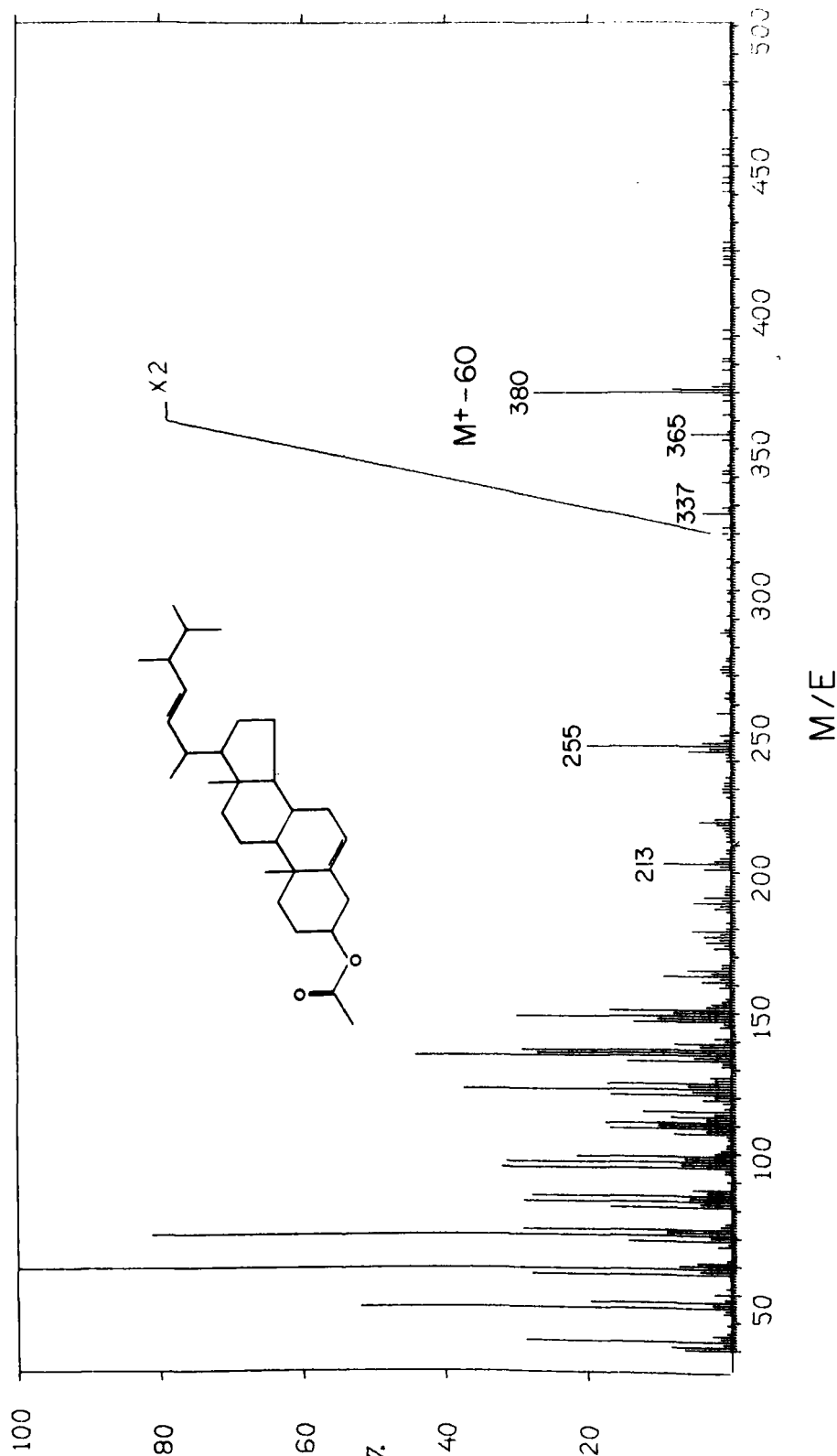


FIGURE 23. Mass chromatograms showing presence of polychlorinated biphenyls (PCB) in tissue extracts of mixed polychaete worms from sediments in Buzzards Bay, Massachusetts.

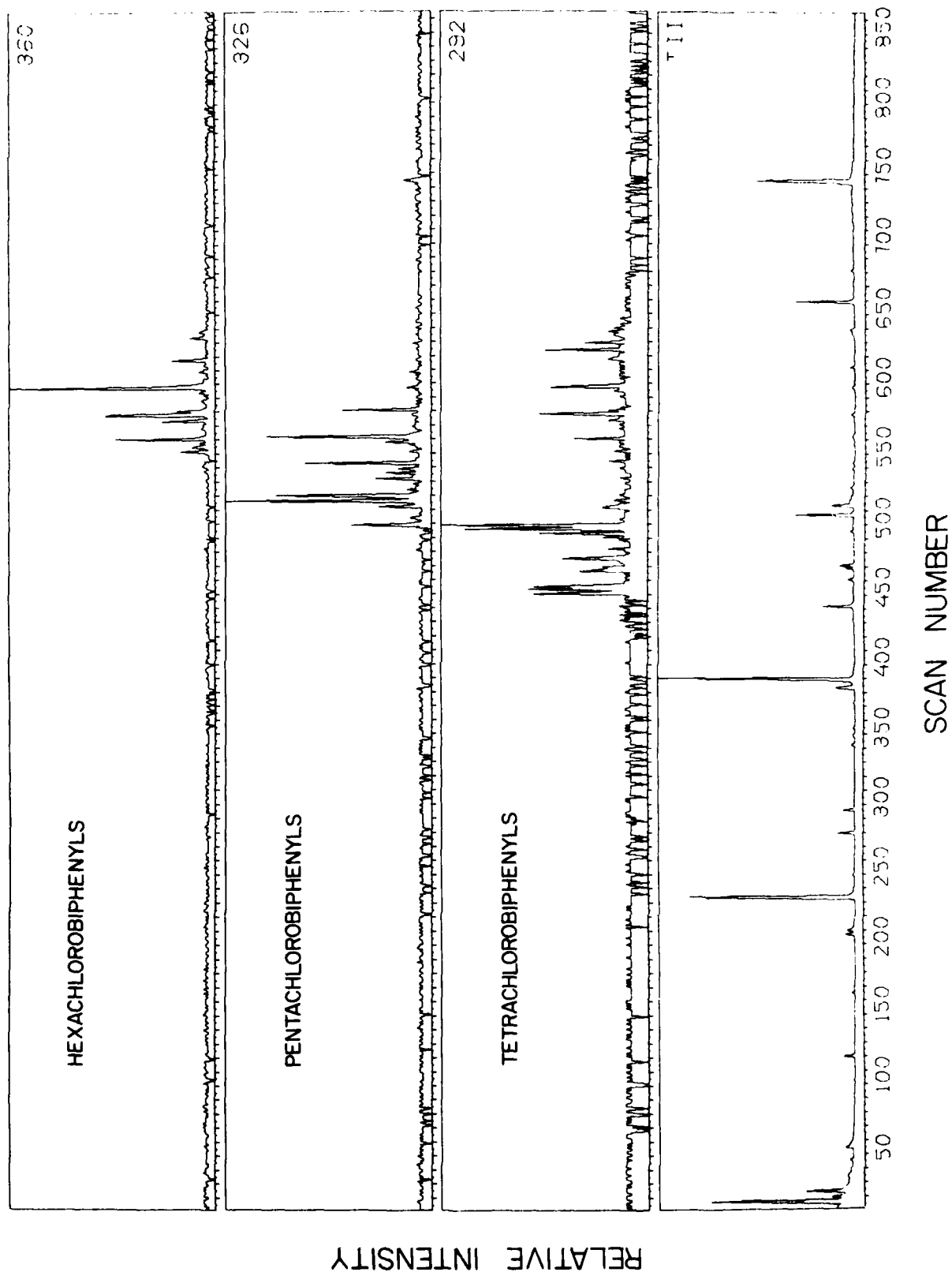




FIGURE 24. Reconstructed gas chromatogram of a total pentane extract of a No. 2 fuel oil/water dispersion used in low level chronic oil addition experiments at the Marine Ecosystems Research Laboratory (MERL), University of Rhode Island. Numbered peaks are n-alkanes. Phenanthrene (PHE) and  $\alpha$ -androstandane ( $\alpha$ -20) are internal standards.

Gas chromatographic conditions: Varian 1400 gas chromatograph; column, SE-52 barium carbonate type, 20 m x 0.32 mm; injector, 270°C; interface 280°C; helium carrier, 0.9 atmosphere; temperature program, 70-250°C at 4°C/min. Mass spectrometer: Finnigan 1015; electron impact, 40 eV.

MERL NO. 2 FUEL OIL/WATER DISPERSION  
08-166-OWD

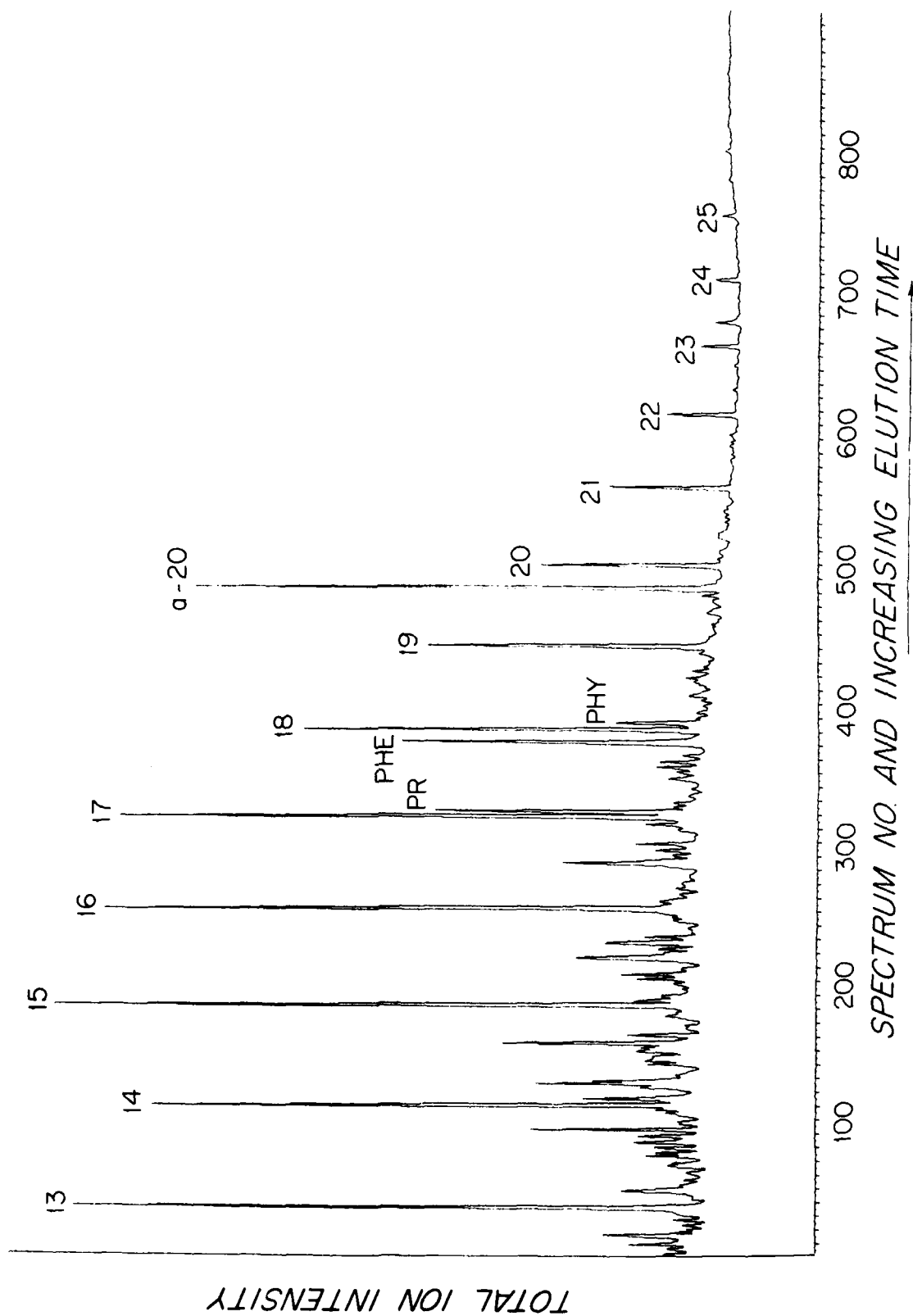


FIGURE 25. Mass chromatogram showing substituted naphthalenes and phenanthrenes in fuel oil/water dispersion of Figure 24.

# AROMATIC HYDROCARBONS-OIL/WATER DISPERSION

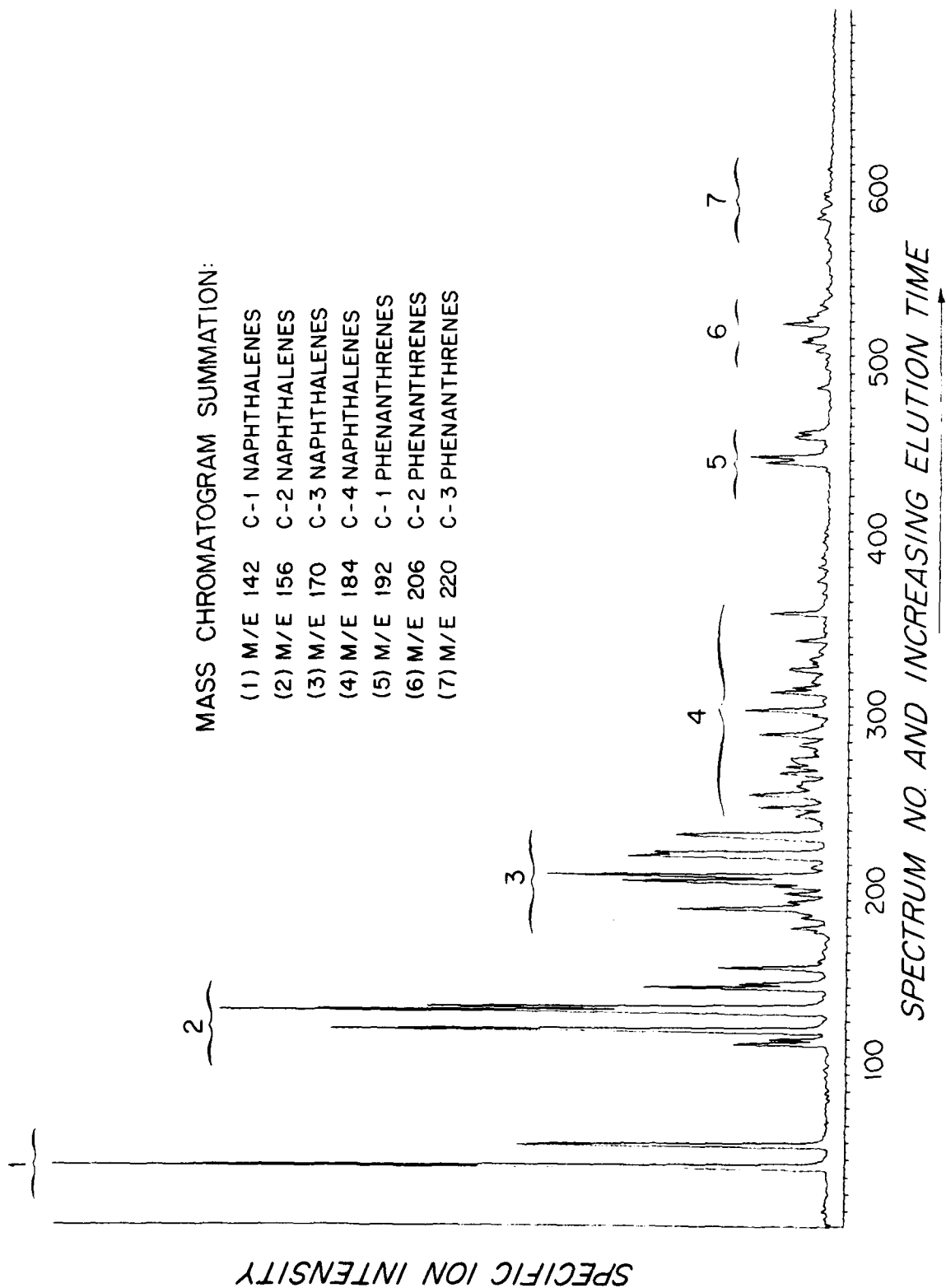
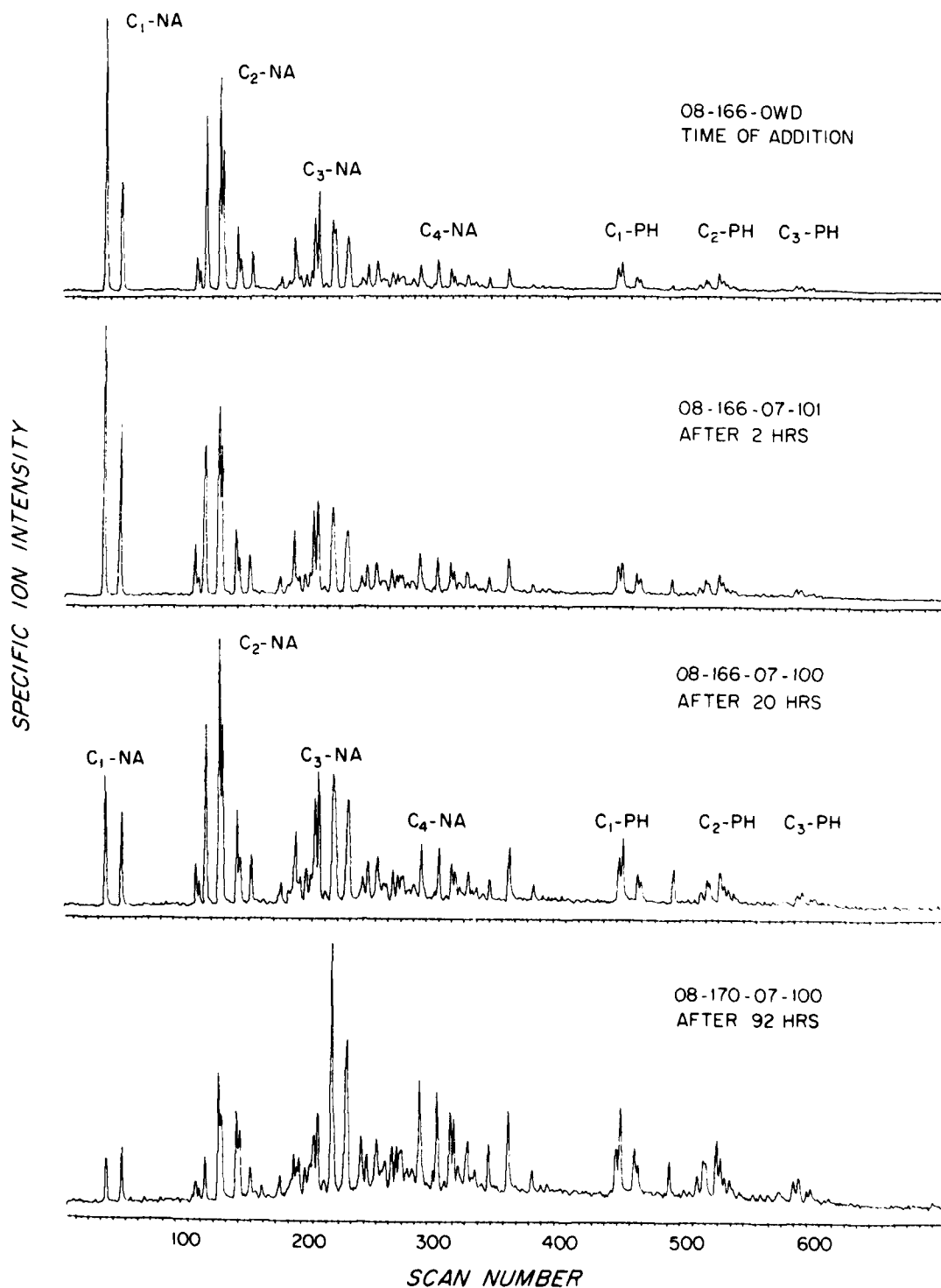


FIGURE 26. Glass capillary GC/EI-MS analyses of MERL tank water samples showing rapid changes in the distributions of naphthalenes and phenanthrenes after addition of an oil/water dispersion. Analytical conditions as given in Figure 24.

NAPHTHALENE / PHENANTHRENE DISTRIBUTIONS  
TANK WATER SERIES



weight material and changes in specific isomer patterns were readily observed within a few days after addition of the oil. Significant accumulations of aromatic hydrocarbons were later detected in benthic organisms as well as in a surface floc which formed above the sediments during the course of the oil addition experiments (Figure 27). Other aromatic hydrocarbons, such as pyrene and fluoranthene, presumably derived from pyrolytic source material originally present in the sediments of Narragansett Bay, were also shown to be present in the experimental fauna (Figure 28).

Similar assemblages of aromatic hydrocarbons have been observed in recent sediments from stations along the northwestern Atlantic continental shelf (FARRINGTON et al., 1979). The GC/EI-MS analysis of surface sediments collected in the New York Bight, for example, indicated that significant concentrations of naphthalenes and phenanthrenes (Figure 29) as well as other aromatic hydrocarbons were present in those sediments.

#### Summary

In a wide variety of applications, the interfacing of high resolution glass capillary chromatography with both electron impact and chemical ionization mass spectrometry has led to significant advantages in GC/MS performance. These advantages include:

- (1) Enhanced sensitivity for trace organics.
- (2) Enhanced selectivity for specific compound classes through controlled fragmentation (CI).
- (3) Increased information yield, particularly regarding isomer distributions.
- (4) Decreased degradation of sensitive sample components.

FIGURE 27. Comparison of substituted naphthalene and phenanthrene distributions in MERL oiled tank water, surface sediment ooze and in the benthic organisms, Ninoe nigripes and Crepidula sp. living at the sediment/water interface.



NAPHTHALENE / PHENANTHRENE ACCUMULATIONS  
SEDIMENT / BIOTA

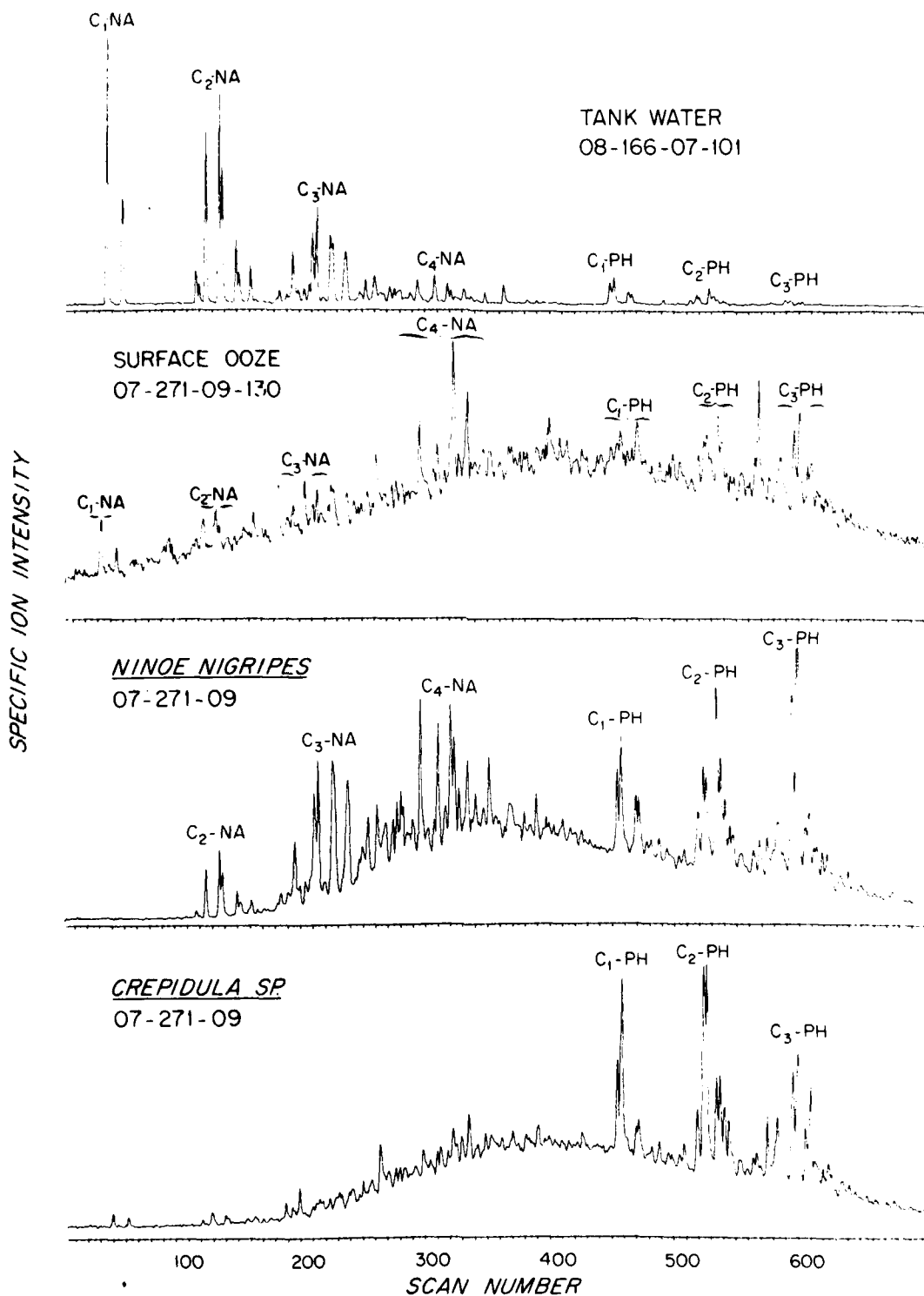


FIGURE 28. Glass capillary GC/EI-MS analyses showing accumulations of fluoranthene and pyrene in MERL tank sediments and bottom organisms.

PYROLYTIC SOURCE PAH-SEDIMENT / BIOTA

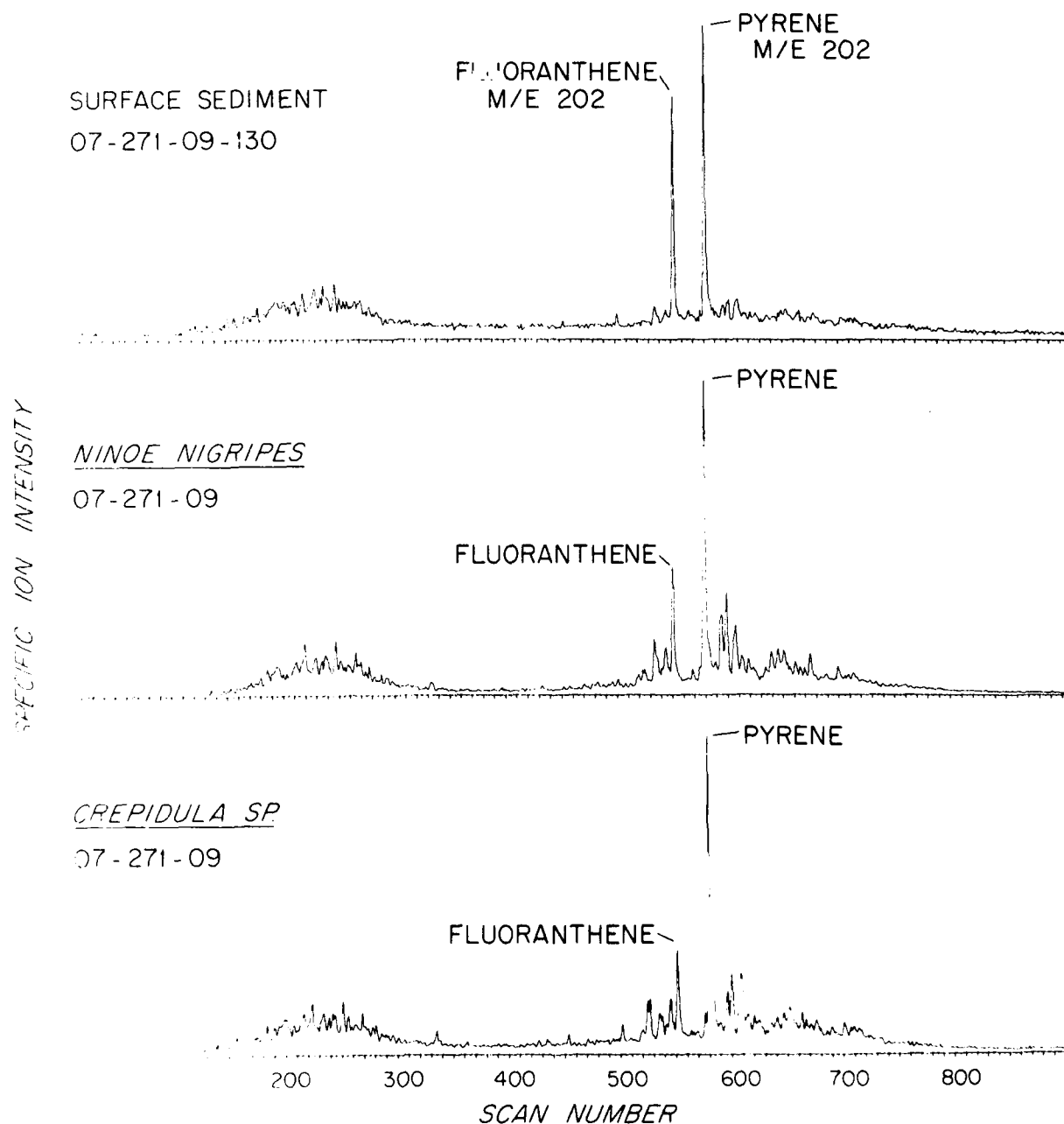
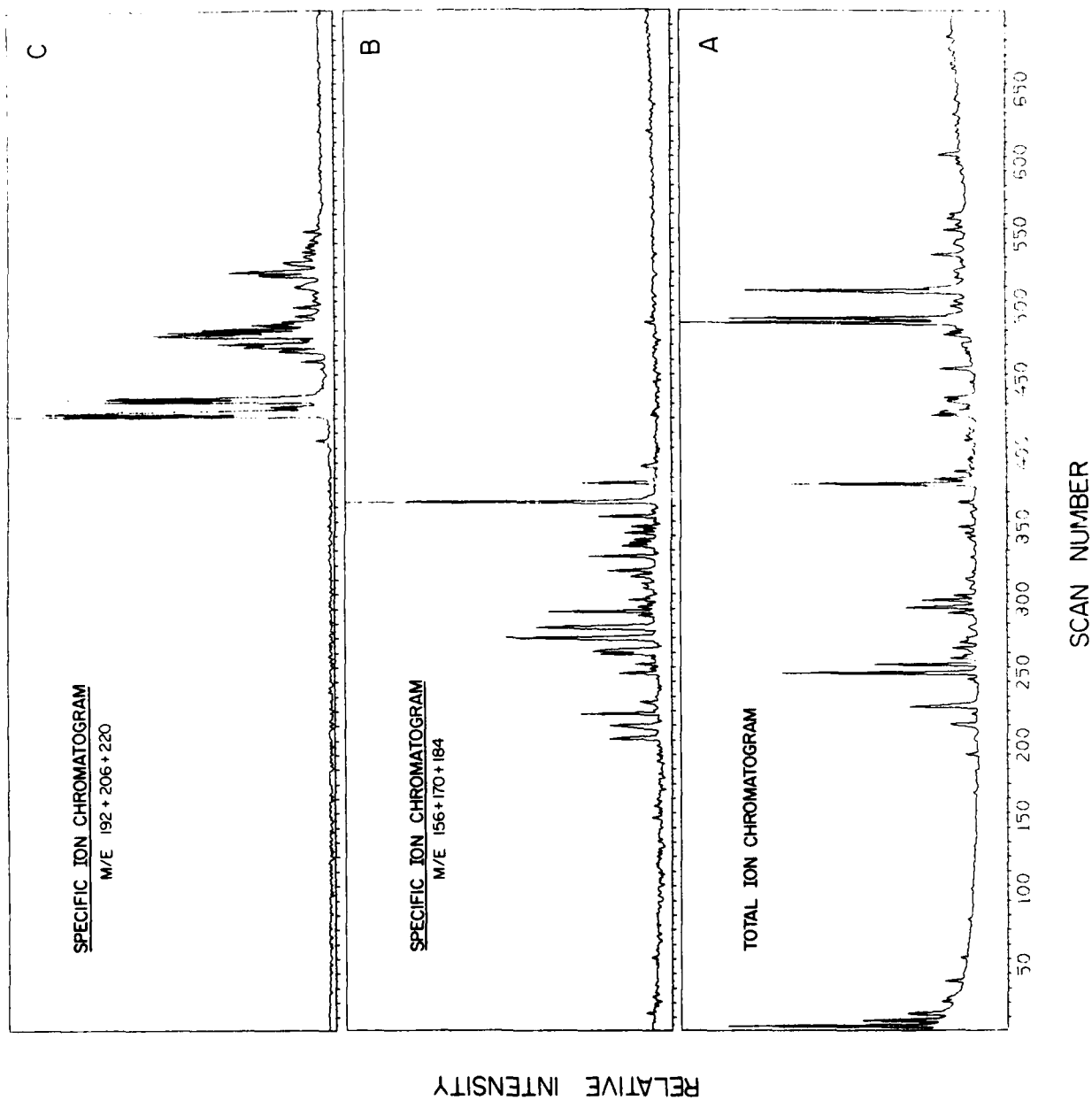


FIGURE 29. Aromatic hydrocarbons in New York Bight surface sediments (OCEANUS 46, Station LL, 0-1 cm): (a) total ion chromatogram, (b)  $C_2$  to  $C_4$  substituted naphthalenes, (c)  $C_1$  to  $C_3$  substituted phenanthrenes. Analytical conditions as given in Figure 24.



ACKNOWLEDGEMENTS

The authors wish to acknowledge the late Dr. Max Blumer for his foresight in recognizing the potential applications of chemical ionization mass spectrometry in marine geochemistry and for making such instrumentation available to the Chemistry Department. We thank Dr. Wolfgang Blum for his willing advice and assistance in the construction and installation of the coaxial interface. We also thank Dr. Kurt Grob for sharing with us his insight and experiences with glass capillary technology and for encouraging us to pursue glass capillary GC/MS as an everyday practical reality.

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Woods Hole Oceanographic Institution WHOI-79-26	<p>GAS CHROMATOGRAPHY-MASS SPECTROMETRY FACILITY: RECENT IMPROVEMENTS AND APPLICATIONS by Nelson M. Frew and Richard M. Sawdo. 85 pages. March 1980. Prepared for the Office of Naval Research under Contracts N00014-66-C-0241; NR 083-004 and N00014-74-C-0262; NR 083-004; for the National Science Foundation under Grants 74-22781, OCE 76-08696, OCE 74-09991, OCE 77-26084, and GC-44224. EPA Grants R80302010 and R8042-15; DOE Contract EE-77-5-02-4256 and the Bureau of Land Management via Interagency Agreement via NOAA 550-1A-7-20.</p> <p>Marine organic and organic geochemical studies require the best available performance in trace analysis of organic compounds in environmental samples. This report briefly outlines some of the recent improvements in the experimental capabilities of the Chemistry Department Gas Chromatography/Mass Spectrometry Facility (GC/MS Facility) from a user-oriented and non-technical viewpoint. 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